PB84-139732

Compatibility of Grouts with Hazardous Wastes

JRB Associates, Inc., McLean, VA

Prepared for

Municipal Environmental Research Lab.
Cincinnati, OH

Jan 84

U.S. Department of Commerce
National Technical Information Service
NTIS

PB84-139732

EPA-600/2-84-015
January 1984

COMPATIBILITY OF GROUTS WITH HAZARDOUS WASTES

by

P.A. Spooner, G.E. Hunt,
V.E. Hodge, and P.M. Wagner

JRB Associates
McLean, Virginia 22102

EPA Contract Number: 68-03-3113
Task: 40-3

Project Officer

H.R. Pahren
Solid and Hazardous Waste Research Division
Municipal Environmental Research Laboratory
Cincinnati, Ohio 45268

MUNICIPAL ENVIRONMENTAL RESEARCH LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
CINCINNATI, OHIO 45268

REPRODUCED BY
NATIONAL TECHNICAL
INFORMATION SERVICE
U.S. DEPARTMENT OF COMMERCE
SPRINGFIELD, VA. 22161

TECHNICAL REPORT DATA

(Please read Instructions on the reverse before completing)

1. REPORT NO.
EPA-600/2-84-015

2.

3. RECIPIENT'S ACCESSION NO.
PB84 139732

4. TITLE AND SUBTITLE
COMPATIBILITY OF GROUTS WITH HAZARDOUS WASTES

5. REPORT DATE
January 1984

6. PERFORMING ORGANIZATION CODE

7. AUTHOR(S)
P. A. Spooner, G. E. Hunt
V. E. Hodge and P. M. Wagner

8. PERFORMING ORGANIZATION REPORT NO.

9. PERFORMING ORGANIZATION NAME AND ADDRESS
JRB Associates
8499 Westpark Drive
McLean, VA 22102

10. PROGRAM ELEMENT NO.
TEJY1A

11. CONTRACT/GRANT NO.
68-03-3113

12. SPONSORING AGENCY NAME AND ADDRESS
Municipal Environmental Research Laboratory--Cin., OH
Office of Research and Development
U. S. Environmental Protection Agency
Cincinnati, Ohio 45268

13. TYPE OF REPORT AND PERIOD COVERED
Final

14. SPONSORING AGENCY CODE
EPA 600/14

15. SUPPLEMENTARY NOTES
Project Officer: Herbert R. Pahren (513)684-7871

16. ABSTRACT

A study was conducted to determine the known information on the compatibility of grouts with different classes of chemicals. The information gathered here can be used as a basis for testing and selecting grouts to be used at specific waste disposal sites with various leachates.

Twelve different types of grouts are included in this study; their inclusion is based on their availability and use in waterproofing and soil consolidation projects. These grouts are bitumen, Portland cement type I, Portland cement types II and V, clay, clay-cement, silicate, acrylamide, phenolic, urethane, urea-formaldehyde, epoxy, and polyester. Sixteen general classes of organic and inorganic compounds are also identified that include the types of chemicals which most probably would be found in leachate from a hazardous waste disposal site. The known effects of each chemical class on the setting time and durability of each grout are identified and presented in a matrix. These data were based on a review of the available literature and contact with knowledgeable persons in industries, universities, and government agencies. The physical and chemical properties, reaction theory, and known chemical compatibility of each grout type are discussed.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group

18. DISTRIBUTION STATEMENT
RELEASE TO PUBLIC

19. SECURITY CLASS (This Report)
UNCLASSIFIED

20. SECURITY CLASS (This page)
UNCLASSIFIED

21. NO. OF PAGES
154

22. PRICE

EPA Form 2220-1 (Rev. 4-77) PREVIOUS EDITION IS OBSOLETE

DISCLAIMER

The information in this document has been funded wholly or in part by the United States Environmental Protection Agency under Contract No. 68-03-3113 to JRB Associates. It has been subject to the Agency's peer and administrative review and has been approved for publication as an EPA document. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

FOREWORD

The U.S. Environmental Protection Agency was created because of increasing public and government concern about the nation's environment and its effect on the health and welfare of the American people. Noxious air, foul water, and spoiled land are tragic testimonies to the deterioration of our natural environment. The complexity of that environment and the interplay of its components require a concentrated and integrated attack on the problem.

Research and development is that necessary first step in problem solution; it involves defining the problem, measuring its impact, and searching for solutions. The Municipal Environmental Research Laboratory develops new and improved technology and systems to prevent, treat, and manage wastewater and solid and hazardous waste pollutant discharges from municipal and community sources, to preserve and treat public drinking water supplies, and to minimize the adverse economic, social, health, and aesthetic effects of pollution. This publication is one of the products of that research and provides a most vital communications link between the researcher and the user community.

The report provides a summary of information on the predicted compatibility of various types of grouts with different classes of chemicals. In certain instances grouts may be used to seal ground masses around uncontrolled hazardous waste sites. Information in the report may be used to provide guidance on the testing, selection, or use of grouts at a particular site.

Francis T. Mayo, Director
Municipal Environmental Research
Laboratory

ABSTRACT

A study was conducted to determine the known information on the compatibility of grouts with different classes of chemicals. The information gathered here can be used as a basis for testing and selecting grouts to be used at specific waste disposal sites with various leachates.

Twelve different types of grouts are included in this study; their inclusion is based on their availability and use in waterproofing and soil consolidation projects. These grouts are bitumen, Portland cement type I, Portland cement types II and V, clay, clay-cement, silicate, acrylamide, phenolic, urethane, urea-formaldehyde, epoxy, and polyester. Sixteen general classes of organic and inorganic compounds are also identified that include the types of chemicals which most probably would be found in leachate from a hazardous waste disposal site. The known effects of each chemical class on the setting time and durability of each grout are identified and presented in a matrix. These data were based on a review of the available literature and contact with knowledgeable persons in industries, universities, and government agencies. The physical and chemical properties, reaction theory, and known chemical compatibility of each grout type are discussed.

Since compatibility data are not complete for each grout type, predictions are made, where possible, for the silicate and organic polymer grouts based on their reaction theory. These results are also presented in a matrix.

To establish the compatibility of chemicals with grouts, a series of laboratory tests should be performed. The two grout properties that must be addressed are permeability of the grouted soil and set time of the grout. No established testing procedures are identified in the literature for determining the effects of chemicals on these grout properties. Fixed-wall and triaxial permeameters, which are used for soil testing, can be utilized for measuring the effects of chemicals on permeability. For set time, there is no single procedure that applies to all grout types for determining set time. Visual observation is the easiest method, though somewhat subjective.

The selection of a grout for a specific waste site depends on its injectability, durability, and strength. These factors relate site hydrology, geochemistry, and geology to grout physical and chemical properties.

This report was submitted in fulfillment of Contract No. 68-03-3113 by JRB Associates under the sponsorship of the U.S. Environmental Protection Agency. The report covers the period April 5, 1982, to November 2, 1982, and work was completed as of November 2, 1982.

CONTENTS

Page

Foreword. iii

Abstract. v

Figures ix

Tables. x

Acknowledgement xi

1. Introduction. 1
    Application of report 2
2. Conclusions 3
3. Recommendations 5
4. Grouting Techniques 7
    Grouting methods. 7
    Grout types 12
    Site characteristics. 14
5. Chemical and Physical Properties of Grouts. 17
    Properties of bitumen grouts. 17
    Properties of cement grouts 20
    Properties of clay grouts 26
    Properties of cement-bentonite grouts 32
    Properties of silicate grouts 33
    Properties of organic polymer grouts. 36
    Properties of other grouts. 53
6. Compatibility of Grouts with Hazardous Wastes 57
    Known compatibility of grouts with classes of chemicals . . 57
    Predicted compatibility of grout with classes of chemicals. 74
7. Grout Compatibility Testing Procedures. 83
    Permeability of grouted sand. 83
    Effect of leachate on grout set time. 95
    Overview of compatibility tests 99
8. Grout Selection 101
    Injectability 101
    Durability. 103
    Other factors 106
    Overview. 106

9. Research Needs. 109
  Grout specifications and applications 109
  Compatibility of grouts with chemicals. 109
  Long-range stability of grouts. 110
  Compatibility testing procedures. 110

References. 111
Bibliography. 119
Appendices

A. Annotated Bibliography. 133
B. Grout Manufactures/Suppliers Information. 137

FIGURES

Figure Page

1 Grout Pipe Layout for Grout Curtain 8

2 Semicircular Grout Curtain Around Waste Site. 9

3 Vibrating Beam Grout Injection. 11

4 Jet Grouting. 13

5 Interactions Between Grouts and Generic Chemical Classes. 72

6 Interactions Between Grouts and Specific Chemical Groups. 75

7 Predicted Grout Compatibilities 77

8 Constant Head Permeameter 85

9 Variable Head Permeameter 87

10 Constant Head and Variable Head Permeameters. 89

11 Variable Head Consolidation Permeameter 90

12 Triaxial Permeameter with Back Pressure 92

13 Constant Head Triaxial Permeameter. 93

14 Schematic of Grouting Test Apparatus. 96

15 Rotational Viscometer 98

16 Grout Selection Process 102

17 Applicability of Different Classes of Grouts Based on Soil Grain Size. 104

TABLES

Table		Page
1	Materials Compatible with Cement.	24
2	Materials Incompatible with Cement.	25
3	Effect on Permeability of Several Undiluted Organic Chemicals on Selected Clays	30
4	Soil/Bentonite Permeability Increases Due to Leaching With Various Pollutants.	31
5	Components of Acrylamide Grouts	38
6	Phenol Resin Grout Products	42
7	Examples of Chemical Within Each of the Chemical Grouts . . .	60
8	Constituents of the General Grout Classes	73
9	Ranges of Values of Various Properties of Selected Grout Types	105
10	Toxicity of Selected Grouts	107
11	Approximate Cost of Grout	108

ACKNOWLEDGEMENT

The authors gratefully acknowledge the constructive contributions of the following reviewers of this report:

Herbert Pahren	U.S. EPA, MERL, Cincinnati, OH. Project Officer
Walter Grube	U.S. EPA, MERL, Cincinnati, OH.
Richard Stanford	U.S. EPA, OERR, Washington, D.C.
Kenneth Stoller	U.S. EPA Region II, New York, NY.
Philip Malone	U.S. Army Engineer Waterways Experiment Station, Vicksburg, MS.
James May	U.S. Army Engineer Waterways Experiment Station, Vicksburg, MS.
Robert Larson	U.S. Army Engineer Waterways Experiment Station, Vicksburg, MS.

The technical contributions of the following individuals were greatly appreciated.

George Alther	International Minerals and Chemical Corporation, IMCORE Division, Detroit, MI.
John Ayers	GZA Corporation, Upper Newton Falls, MA.
Donald Hentz	Federal Bentonite, Belle Fourche, SD.
Dr. Raymond Krizek	Northwestern University, Chicago, IL.
Glen Schwartz	Engineered Construction International, Inc. Pittsburgh, PA.

Our appreciation is also extended to the numerous other individuals who were contacted on matters related to this report.

SECTION 1

INTRODUCTION

The purpose of this project is to compile data on the compatibility and durability of grouts in the presence of hazardous wastes and leachates, and to summarize the test procedures available to measure durability.

Grouting has been used for years by the construction industry as a technique for treating ground masses to consolidate and seal them. The principal use for grouting has been for large dam and tunneling projects. Although grouting is still very much an art rather than an exact engineering discipline, a great deal has been published on the properties, applications, and testing of grouts. But, nearly all of this information however, has focused on the use of grout in construction rather than in remedial work at hazardous waste disposal sites. In addition, the testing procedures in current use are not yet standardized and do not deal directly with the ability of grouts to set up in and withstand attack from hazardous wastes and leachates.

Consequently, this study centered on collecting, organizing, and analyzing existing published and unpublished information on the compatibility and durability of grouts with various classes of chemicals. Published literature was identified by undertaking a computer literature search as well as tree searches. Universities were contacted in order to collect information from research programs. Grout manufacturers, grout supply companies and grout installation firms were contacted for information on grout compatibility and the physical/chemical characteristics of the grouts they manufactured or used. Information gained by contacting industry was limited primarily due to the lack of specific compatibility information. In a few cases, though, information was available but could not be released due to its proprietary nature. Where sufficient information was not available, compatibility determinations were based on the chemistry and reaction theories of the various grouts and chemical classes.

This report reviews the properties of the grouts in use today and summarizes their chemical compatibility. Included is an overview of grouting and a discussion of grout compatibility testing procedures. Also addressed are the factors to be considered in grout selection and the grout selection process. The report also identifies areas that need more research for a full evaluation of grout compatibility with hazardous materials. Appendix A presents abstracts of key information resources, and Appendix B presents a listing of grouts and the companies which manufacture them.

APPLICATION OF REPORT

A key aspect of this report is a series of matrices presenting the known and predicted effects of different chemical groups on the set time and durability of the various grouts currently in use. The chemical groupings used in these matrices contain most of the organic and inorganic compounds found in hazardous wastes and associated leachate. For the purposes of this report, the compounds contained in these wastes and leachates are assumed to act independently. Since a detailed chemical characterization is assumed to have been performed before containment systems are evaluated, the individual components will be known.

This report presents the basic information for selecting grouts based on their compatibility with chemicals, it does not specifically address the stability of the grouts with respect to ground conditions, other factors that affect durability, nor grout-specific properties that are ultimately influential in the selection of grouts. These topics are briefly summarized in the descriptions of grout properties, however.

The concentration of chemicals is an important factor in their compatibility with grouts, but much of the available data do not specify concentrations. If concentrations are specified, they generally refer either to dilute or high strength solutions without giving actual concentrations.

Furthermore, chemical compatibility data for the chemical grouts often consisted of data for mortar or pipe-sealing applications rather than for soil sealing applications. Though the compatibility would be comparable for the different formulations, the chemical concentrations in contact with mortar would be significantly higher than for soil grouts.

Other factors affecting the applicability of the compatibility data are the variability of grouting formulations and the amount of conflicting data on these formulations. The grouting formulations may be varied to meet different needs and conditions through the addition of setting agents, accelerators, retardants, and other chemicals. These additional materials have a distinct impact on the properties of grout and its behavior during setting as well as the chemical compatibility of the set grout. In researching the grouts in use and their properties, much conflicting data were encountered in the literature and in discussions with knowledgeable people in this industry. This was particularly true regarding the types of grouts actually in use, their constituent materials, and their properties. Thus, this report consolidates the available information and presents a general summary that represents the salient features of each grout type and its properties.

SECTION 2

CONCLUSIONS

This report permits the following conclusions regarding grouts in general and their compatibility with hazardous wastes.

Little actual chemical compatibility testing has been performed on grouts. Much of the data presented here have been taken from related uses of similar materials and not specifically from the testing of grouts in contaminated soils. Significant data were collected, for example, from research in waste solidification and encapsulation techniques. Furthermore, few documented cases exist of the use of grouts and grouting technology for hazardous waste site remediation.

Laboratory testing of grout/chemical compatibility centers on evaluating two general factors: the effect of chemicals on grout set time and how long the grout will remain effective after prolonged exposure to the chemicals. Protocols for conducting these particular tests have yet to be developed.

Selection of a grout for a particular purpose depends primarily on site characteristics and the grout's injectability, strength, permeability, and durability. In addition, costs and toxicities of grouting materials are major factors.

Suspension grouts (cement, clay, and cement/clay) are the most common, accounting for approximately 95 percent of all grout used. Silicate grouts are the most commonly used chemical grouts, followed by acrylamides and urethanes. Other minor grout types are used in less than 1 percent of grout applications.

SECTION 3

RECOMMENDATIONS

Recommendations regarding information and concepts presented in this report generally represent research that is needed to understand and quantify further the grout and chemical compatibility issue. Briefly, these areas of needed research include: grout specifications and applications, compatibility of grouts with chemicals, long-term grout stability, and compatibility testing procedures. In addition to laboratory studies, pilot scale evaluations of the most promising systems are recommended.

These research needs are specifically addressed in Section 9. Among the recommended research topics are:

- Identification of specific grouting formulations and their properties
- Chemical effects on grout setting and durability
- Effects of various chemical concentrations on grouts
- Effect of chemical mixtures
- Effect of groundwater
- Long-range stability of grouts
- Selecting compatibility testing procedures.

SECTION 4

GROUTING TECHNIQUES

Grouting is a process by which a fluid material is pressure injected into soil, rock, or concrete to reduce fluid movement and/or to impart increased strength. Grouts accomplish this through their ability to permeate voids, and gel or set in place. This section provides an overview of grouting methods and procedures that can be used at waste disposal sites, general grout types and the site specific factors affecting grout selection.

GROUTING METHODS

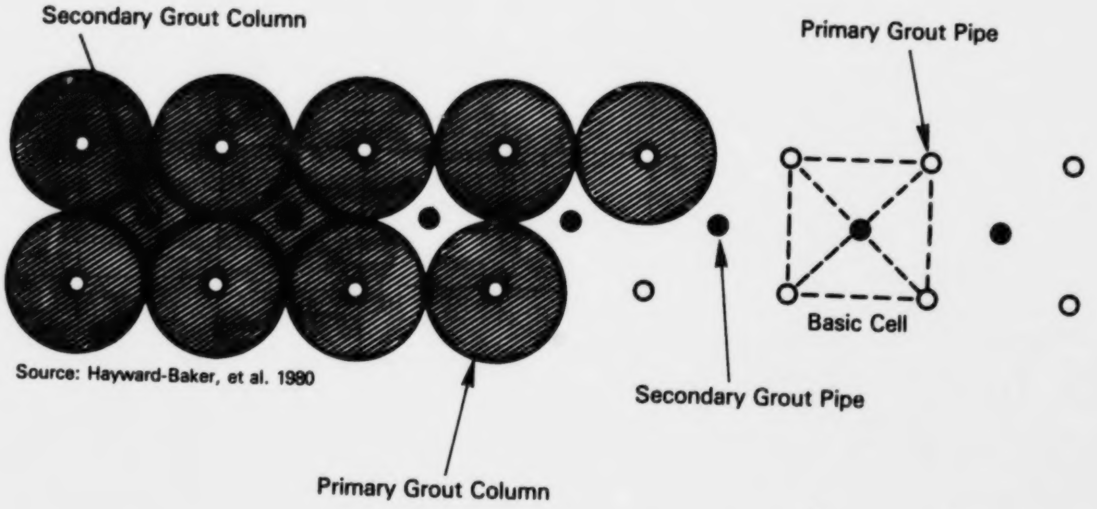
Grouting in conjunction with waste disposal sites, while not common, can be accomplished by several methods to meet various goals. In many cases, more effective or cost-efficient alternatives are available. However, there are specific applications for grouts in cases where alternatives, such as slurry trenches, are not practical. Grouting methods that can be used include:

- Curtain grouting
- Jet grouting
- Area grouting
- Contact grouting
- Large void sealing (Bowen 1981, Caron 1982).

Each of these methods and the procedures used are briefly discussed below.

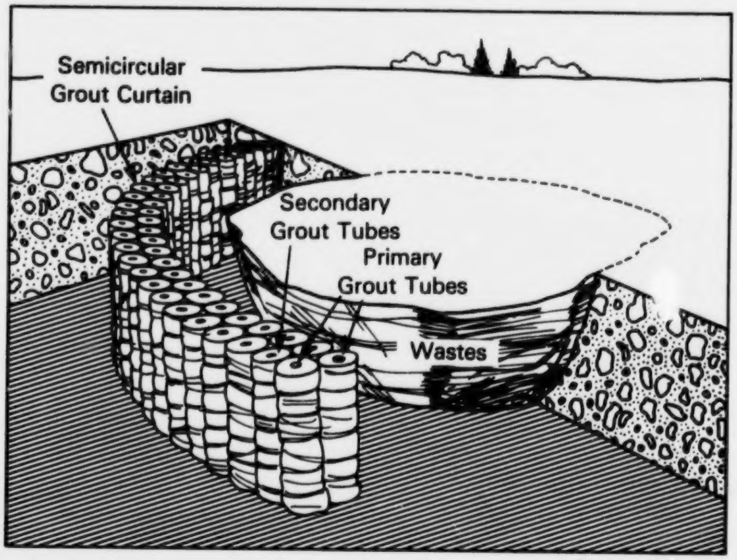
Curtain Grouting

A grout curtain is an underground cut-off or barrier formed by injecting grout through grout pipes in a specific pattern. The grout pipes are placed down bore holes, typically in triple rows of primary and secondary holes (see Figure 1). Starting with the primary holes, grout is injected in "pillows," working upward or downward in stages. This procedure forms rows of primary columns which, when set, are tied together by injecting the secondary columns (Hayward Baker Company et al. 1980). Grout curtains are keyed into impermeable substrates. Figure 2 illustrates the wall or curtain formed by the coalescing columns.


Secondary Grout Column
Primary Grout Pipe
Basic Cell
Secondary Grout Pipe
Primary Grout Column

Source: Hayward-Baker, et al. 1980

Figure 1. Grout Pipe Layout for Grout Curtain


Semicircular Grout Curtain
Secondary Grout Tubes
Primary Grout Tubes
Wastes

Source: JRB 1982

Figure 2. Semicircular Grout Curtain Around Waste Site

There are several basic techniques that can be utilized to form a grout curtain. These include:

- Stage-up method
- Stage-down method
- Grout-port method
- Vibrating beam method (Hayward Baker Company et al. 1980, Tiedemann and Graver 1982).

In the stage-up method, the borehole is drilled to the full depth of the wall prior to grout injection. The drill is then withdrawn one 'stage,' leaving several feet of borehole exposed for injection of the desired volume of grout. When injection is complete the drill is withdrawn further and the next stage is injected (Hayward Baker Company et al. 1980).

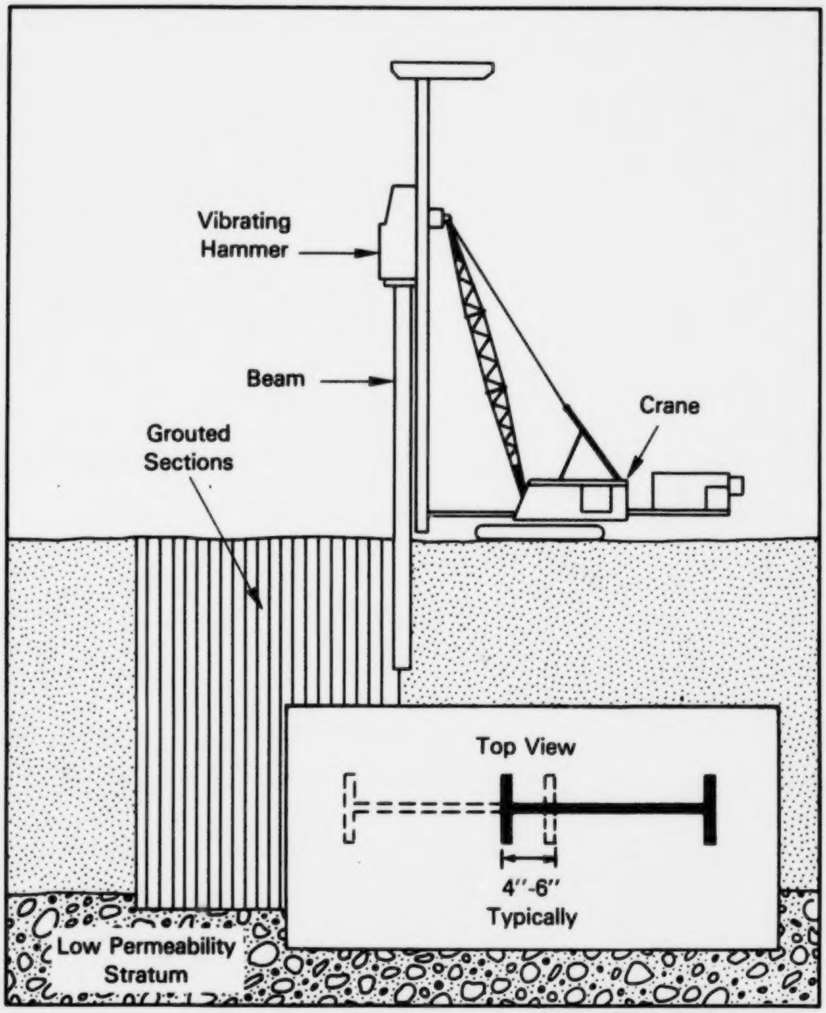
The next technique, stage-down grouting, differs from stage-up grouting in that the injections are made from the top down. Thus, the borehole is drilled through the first zone that is to be grouted, the drill is withdrawn and the grout injected. Upon completion of the injection, the borehole is redrilled through the grouted layer into the next zone to be grouted and the process is repeated (Hayward Baker Company et al. 1980).

The grout port method (also known as the tube a'manchettes) utilizes a slotted injection pipe that has been sealed into the borehole with a brittle portland cement/clay mortar jacket. Rubber sleeves cover the outside of each slit (or port), permitting grout to flow only out of the pipe. The injection process is started by isolating the grout port in the zone to be injected with a double packer. A brief pulse of high pressure water is then injected into the port, rupturing the mortar jacket. Grout is then pumped into the double packer, it passes through the ports in the pipe, under the rubber sleeve and out through the cracked mortar jacket into the soil. (Guertin and McTigue 1982)

The vibrating beam is an alternate method of placing the grout in such a way as to form a low permeability wall. In this method, a large I-beam is worked vertically into the soil to the desired depth using a vibrating hammer, then raised at a controlled rate. As the beam is lowered and raised, a grout is pumped through a set of nozzles mounted in its leading edge, filling the cavity formed. When the cavity is completely filled, the beam is moved along the direction of the wall, leaving a suitable overlap to insure continuity, and the process is repeated (Harr, Diamond, and Schmednecht [not dated]). Figure 3 shows the steps involved in forming a vibrating beam cut-off wall.

Jet Grouting

Jet grouting is a method of cutting an opening in soil or soft rock using a high pressure nozzle (Caron 1982). Once an opening has been made, using either water or grout as the cutting fluid, grout sets in the voids to


Vibrating Hammer
Beam
Crane
Grouted Sections
Top View
4"-6" Typically
Low Permeability Stratum

Source: Soletanche (Unpublished)

Figure 3. Vibrating Beam Grout Injection

form a low permeability zone, Figure 4. Using this technique, it is theoretically possible to emplace a grout liner beneath a waste site. Although this may require jetting through a hole drilled down through the wastes, advances in directional drilling techniques may soon make this method more practical.

Area Blanket Grouting

Area grouting is a low pressure technique used to form a grout "blanket" in near surface soil materials. This is accomplished by injecting grout into a series of closely spaced injection holes placed in a grid pattern. This is usually performed to reduce infiltration, prevent erosion losses, or stabilize soils for heavy machinery bases (Bowen 1981). Area grouting may be adaptable to in situ waste immobilization by injecting into the wastes, depending on the compatibility of the wastes with the grouts.

Contact Grouting

Contact grouting is low pressure injection of grout to seal surface cracks or other voids. This technique may be used to patch cracked concrete in dams or dikes or reduce leakage, and to seal the sides of excavations to reduce water infiltration (Bowen 1981). Applications of contact grouting to long term waste site remediation are limited.

Large Void Sealing

Grouts have long been used for sealing large voids in rock and other materials, mainly in conjunction with dam or tunnel projects (Bowen 1981). Adaptations of this method to waste disposal sites could include forming a tie-in between a slurry wall and highly fractured or weathered bedrock, and sealing leaks in aquitards resulting from exploration bore holes or improperly installed wells. In sealing voids with a large water flow through them, an extremely short and controllable set time may be required to avoid washing the grout out before it seals (Sommerer and Kitchens 1980).

GROUT TYPES

There are three general classes of grout utilized today. These include:

- Suspension grouts
- Chemical grouts
- Bituminous grouts (Tiedemann and Graver 1982, Bowen 1981).

Suspension grouts are the most common type of grout and include coarse grouts which contain particles in suspension. Cement, clay, and cement-clay grouts are in this category. These materials are usually the more viscous of the available grouting materials and have the largest particle size. Thus, these grouts are restricted to use in the grouting of fractured rock or coarse grained material.

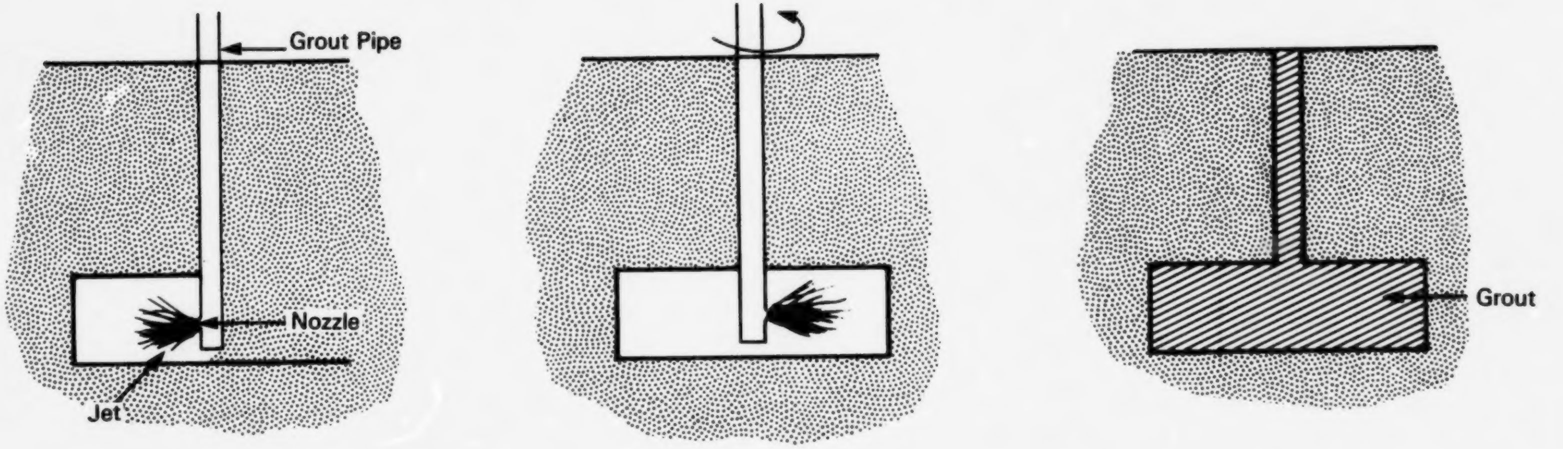

Grout Pipe
Nozzle
Jet
Grout

Figure 4. Jet Grouting

Chemical grouts rely on polymerization reactions to form hardened gels. They have initially low viscosities and thus can be used in finer grained, cohesionless soils as well as a secondary treatment for grouting of coarse soils and rock fissures. Some chemical grouts such as some urathane, can be suspentions which undergo polymerization to form a gel. This class of grouts is comprised of two subclasses, silicates and organic polymer grouts.

Bituminous grouts can either be emulsions of bitumen in water or asphalts. These grouts can be used to seal soils, fill rock cavities, or construct thin cut-off walls.

SITE CHARACTERISTICS

The success of a grouting project depends on thorough investigation and characterization of the site in question, and selection of a grout that is suited to the particular site. The following is a discussion of the types of geotechnical information required to plan a grouting project and how this information can affect grouting.

Soil and Rock Characteristics

The nature of the earth materials at a site will influence greatly the type of grout to be used. If soil materials are to be grouted, the characteristics that must be determined include:

- Permeability
- Porosity
- Particle size distribution.

Permeability will influence the selection of grout type (particulate or chemical) to be used, the allowable viscosity, and the required injection pressures (Bowen 1981). The porosity, or voids ratio, will give an indication of the amount of grout a unit volume of soil will "take," and how rapidly grout may be injected (Herndon and Lenahan 1976a). The particle size distribution indicates, among other things, the presence of large particles which could interfere with grout injection. The type of grout recommendations for various grain uses sizes is discussed more specifically in Section 8.

To effectively seal voids in rock by grouting, the nature and extent of the voids must be well characterized. The size, shape, and distribution of cracks, solution channels, or other rock openings will determine allowable grout viscosities, appropriate set time, and required grout volume. (Tallard and Caron 1977b).

Geochemical Characteristics

The geochemistry of a site, including that caused by waste disposal, can be extremely important to the success of a grouting project. Among the geochemical data that should be determined during a design phase site investigation are the nature and extent of wastes and leachates at the site, and presence of soil or rock layers (such as salt deposits) that may significantly impact grout solution chemistry.

SECTION 5

CHEMICAL AND PHYSICAL PROPERTIES OF GROUTS

The grouts used for soil consolidation and groundwater control are emulsions, polymers, and particle suspensions. These materials are generally water based solutions of sufficiently low viscosity to allow them to penetrate rock and soil voids. Particulate grouts, composed of cements, clays, or mixtures of the two, constitute approximately 95 percent of the grout used. The remaining 5 percent is primarily silicate grout, although bitumen and organic polymer grouts do see some limited use for water sealing. Because of the unique characteristics of different grouts, these traditional breakdowns of grout usage may not correspond to grout usage at hazardous waste sites.

This section describes the properties of these grouts. The properties include: chemical composition, reaction theory (gelation or set mechanisms), physical nature, toxicity, and compatibility/incompatibility data. In addition, situations where these grouts have been used are summarized.

PROPERTIES OF BITUMEN GROUTS

Bitumen grouts can be of several types including bitumen/water emulsions, heated bitumen and mixtures of bitumen with other materials. Bitumen or asphalt emulsions are direct emulsions in water, with water being the major component. These emulsions have a variety of uses including surface and subsurface waterproofing applications. Emulsions are typically used for fine materials such as sand or in finely fissured materials. Hot bitumen grout has been used in coarse soil formations, however, it is difficult to use because it is necessary to preheat the ground with steam, and the heating equipment for the grout require precise temperature regulation (Tallard and Caron 1977a). Because of the preheating and temperature control requirements as well as the short range of penetration in fine soils, heated bitumenous materials appear to have limited use as grouts (Tallard and Caron 1977a). Finally, bitumen can be mixed with other compounds to yield a usable grout. A commercially available grout, ASPEMIX®, used in conjunction with the vibrated beam injection technique is of this type.

Chemical Composition and Reaction Theory

Bitumen or asphalt emulsions consist of bitumen, water, and an emulsifier. Bitumens are viscoelastic materials containing high molecular weight hydrocarbons (Kirk-Othmer 1978a). When dispersed in water, bitumens yield an emulsion with a low viscosity suitable for injection (Tallard and Caron 1977a). Typical emulsions include bitumens; bitumen, soap, and casein; and bitumen with fillers such as clays (Bowen 1981).

Emulsions are stabilized by the emulsifiers, which delay molecular aggregation and increases in viscosity (Kirk-Othmer 1978a). The emulsifiers are polar and determine whether the resulting emulsion is cationic or anionic (Bowen 1981). For example, amine chains are often used as acid emulsifiers to yield cationic emulsions (Bowen 1981, Kirk-Othmer 1978a). Further, the emulsifiers for these emulsions should be water soluble so as to mix with the emulsion and should properly balance the hydrophilic and lipophilic properties of the water and bitumen components of the emulsion, respectively (Koehmstedt, Hartley, and Davis 1977).

As a grout, bitumen emulsions separate upon contact with earth materials; the more viscous emulsion components settle and fill the pores and fissures in the earth material. The breakdown of bitumen emulsions can occur through loss of stabilizing agents, addition of destabilizing agents, or adsorption of emulsifying water. In the first method, a stabilizing agent is eliminated through decomposition or absorption by fine soil material. Direct breakdown is difficult to control and often occurs too quickly or too slowly (Tallard and Caron 1977a). In the second method, destabilizing agents (electrolytes or hydrolyzable esters) may be added to the emulsion either before or after it is injected to promote breakdown and flocculation of the emulsion (Bowen 1981, Tallard and Caron 1977a). When destabilizing agents are added, a one step method (addition of additives prior to injection) is preferable (Tallard and Caron 1977a).

ASPEMIX®, a grout used with the vibrated beam injection method is a bitumen mixture containing cement, asphalt emulsion, fly ash, sand and water. This mixture is pumpable and once injected will set into a solid mass (Slurry Systems (not dated)).

Bitumen Grout Properties

As described previously, bitumen alone is a viscous liquid. Upon emulsification in water, a low viscosity emulsion is obtained (Tallard and Caron 1977a); the viscosity is a little higher than that of water (Bowen 1981). The viscosity of the emulsion is primarily controlled through the ratio of bitumen to water.

The set time of bitumen grout will vary depending on the method used to achieve a breakdown of the emulsion. Set time is further controlled by the emulsifer present in the grout (Koehmstedt, Hartley, and Davis 1977).

Bitumen grout is known to have long term stability (Tallard and Caron 1977a). Oxidation and aqueous leaching of oxidation products are the primary causes of degradation; these mechanisms have largely been studied for surficial applications of asphalt. Oxidative processes include microbial action and sunlight; there is little evidence of anaerobic bacterial oxidation (Hartley et al. 1981). Upon aging, the viscosity of the bitumen emulsion may increase due to increased rigidity (Kirk-Othmer 1978a).

The bitumen used as grout typically consists of a coal tar or asphalt base (Tallard and Caron 1977a). These materials consist of high molecular weight hydrocarbons which, if leached, could be toxic.

Grout/Chemical Interactions

Bitumen or asphalt is resistant to most chemicals. Inorganic chemicals (except concentrated acids), dilute acids, lower alcohols, glycols, and aldehydes will not affect bitumen.[1] ASPEMIX, an asphalt-based slurry used in vibrating beam constructed slurry walls, has been found in the short term to be resistant to paint thinner and hazardous waste site leachate containing various chemicals or brine (Slurry Systems 1982). In particular, ASPEMIX appears to be resistant to coal tar, which contains dimethylnapthalene, methylnapthalene, and pyrene.[2]

Asphalt is not compatible with concentrated mineral acids. Most polar and nonpolar solvents will dissolve asphalt as will chlorinated, aliphatic, and aromatic hydrocarbons. Ketones will also affect asphalt and phenols may slowly degrade asphalt.[1] Salts and organic matter in the earth can prevent proper formation of a seal between bitumen or asphalt and soil. In addition, sea water will cause bitumen emulsions to effloresce and become powdery (Ingles and Metcalf 1973).

Some liners for hazardous waste sites consist of an emulsified asphalt membrane. In general, materials reported to be detrimental to emulsified asphalt membranes include organic substances, highly ionic wastes, and waste containing salts, strong acids, and strong bases (Haxo 1980).

Areas of Application

The primary application of bitumen grouts is to reduce the permeability of fine sands, fine soils (clayey sand), or finely fissured masses. This type of grout is not suitable for coarse soils because a poorly gelled grout may draw away from the coarse material because of weak cohesion of the grout to the soil material resulting in an ineffective seal (Tallard and Caron 1977a). Bitumen grout may be applied in combination with cement (Bowen 1981).

ASPEMIX®, has have been used to construct containment barriers at several hazardous waste sites. This application is quite recent therefore long term evaluations are not available. In the short term, this material has proven to be successful in containing leachate (Slurry Systems 1982).

---

[1] Puzinaurkas, V.P., Asphalt Institute, Washington, D.C. Verbal communication with G. Hunt, JRB Associates, August 25, 1982.

[2] Drozda, A.J., J.E. Brenneman Co., Philadelphia, PA. Written communication with R. McGillen, Ecology and Environment, Pennsauken, NJ. September 24, 1981.

PROPERTIES OF CEMENT GROUTS

Cement has been used prior to clays for grouting applications (Bowen 1981). Cement grouts utilize hydraulic cement which sets, hardens, and does not disintegrate in water (Kirk-Othmer 1979). Because of their relatively large particle size, cement grouts are suitable for rock rather than soil applications (Bowen 1981). Additions of clay or chemical polymers can, however, improve the range of usage.

Chemical Composition and Reaction Theory

Cement grouts consist of Portland cement and water. Several types of Portland cement are available; the types used in soil grouting include Type I (ordinary Portland cement), Type II (modified Portland cement, moderate sulfate resistance), and Type V (low alumina, sulfate resistant). Fillers such as clay, sand, ground slag, or pozzolans, and additives such as chemical polymers may be mixed with the cement to change the characteristics of the grouts and improve their resistance to deleterious chemicals (Littlejohn 1982, Bowen 1981).

When cement, water, and aggregate materials, such as sand and gravel are mixed together in the proper proportions and allowed to harden, they form concrete. The hardening process, during which the cement mixture changes from a slurry to a solid, occurs as a result of the selective hydration of the calcium silicates. This hydration causes an increase in the strength and durability of the concrete. The increase in strength over time is referred to as the curing process (Neville 1973).

Portland cement is made from calcium oxide, alumina, and silica. The calcium oxide is derived from heated limestone. Clay or shale provide the alumina and silica. Gypsum is added to the mixture to prevent excessively rapid setting. When readily available, iron oxide or ground blast furnace slag may also be added (Bowen 1981, Neville 1973). The chemical substances found in Portland cement are tricalcium silicate (45 percent) and dicalcium silicate (27 percent) as well as lesser amounts of tricalcium aluminate and tetracalcium alumino-ferrite (Littlejohn 1982, Ingles and Metcalf 1973). Magnesium oxide, free lime, and silica are also present in minor quantities (Littlejohn 1982). The calcium silicates however, are the major cementitious compounds in cement (Neville 1973).

Various materials (organic and inorganic) may be added to cement grout to achieve special characteristics or to control grout properties. Special additives include agents to prevent excessive bleeding, set time accelerators and retarders, and expansion agents (Littlejohn 1982). Latexes or water soluble polymers may be added to achieve special properties (Kirk-Othmer 1979). Calcium chloride may be added as an accelerator, however, it may cause increased shrinkage upon drying (Littlejohn 1982). Sand may be added so that cement grouts may be used to seal coarse materials (Bowen 1981). Clays can be added to stabilize the cement and reduce bleeding while pozzolans or clay may be added to improve alkali resistance (Littlejohn 1982, Bowen 1981). Polyhydric alcohols can be added to provide acid-resistance (Farkas and Szwarc 1949). Protective colloids such as gelatin, agar, and ammonium stearate may be added as stabilizers in cement grouts (Bowen 1981).

Upon addition of water, the silicates and aluminates in cement form hydration products which have low water solubility (Neville 1973). The calcium silicates form gels of mono- and di-calcium silicate hydrate. The insoluble calcium silicate hydrate crystallizes to form a matrix within which the remaining hydration products form (Ingles and Metcalf 1973, Neville 1973). The resulting cement gel is considered to be a finely dispersed physical mixture of copolymers of hydrates (Neville 1973).

Cement Grout Properties

The physical properties of both fresh and cured cement mixtures depend primarily on the water-cement ratio, the degree of hydration of the cement, and the types of additives used. In addition, the strength and durability of the cured material are affected by the temperature and humidity conditions during curing and the length of curing time allowed.

Viscosity--

The amount of water added to the cement controls the viscosity of the cement grout. As the water-cement ratio increases from 0.4 to 0.7, the viscosity decreases from 5,000 to 500 CentiPoise (cP). The viscosity can also be reduced through the addition of certain organic admixtures (Kirk-Othmer 1979).

Setting--

The setting process occurs in two stages. During the initial set, the fluidity of the grout decreases until it is no longer pumpable. This is considered the set time. The final set occurs as the grout hardens and increases the strength. The time to achieve the final set is referred to as the hardening time (Littlejohn 1982).

The various components of cement grouts set at different rates. These rates vary from a "flash set" (tricalcium aluminate) to several hours (tricalcium silicate and dicalcium silicate) (Littlejohn 1982). Setting normally takes approximately 6 hours, however, the presence of impure calcium silicates can modify this (Kirk-Othmer 1979). Other cement types can set much more rapidly. For example, resin gypsum cement sets in 30 to 90 minutes (Bowen 1981).

In some instances, it is desirable to lengthen the time required for a cement grout to set. A number of substances may be used to increase the set time. These include: organic materials, silt, clay, coal, lignite, sulfates and a number of salts of sodium and metals (Fung 1980, Thompson, Malone, and Jones 1980). Set times may also be lengthened by increasing the water-cement ratio. In addition, sugar or tartaric acid (0.04%) can be used to double the set time (Littlejohn 1982). Special additives such as calcium sulfate may be added to control set time or to resolve setting problems (Kirk-Othmer 1979, Neville 1973).

In excess, some of these materials may entirely prevent the cement grout from setting.

Durability--

While cement mixtures are relatively durable under normal conditions, they can be subject to deterioration as a result of deficiencies in grout quality, drying conditions, chemical attack, and temperature fluctuations (Littlejohn 1982).

Grout quality can be diminished by adding excessive amounts of water. Increasing the water-cement ratio can greatly increase the permeability of the concrete by increasing the number of capillary spaces thereby promoting penetration of solutions (ACI Committee 515 1979, Kirk-Othmer 1979). Further, all cement grouts expel bleed water, particularly those with high water-cement ratios. The bleeding process can lead to accumulation of water on the grout surface, a decrease in grout strength, and an increase in the lateral permeability of the grout curtain (Bowen 1981).

Excessively rapid drying can decrease the quality of a grouted cut-off wall. Rapid drying promotes cracking of concrete, soil cement, and cement grouts. Soil cement which is a mixture of soil, cement, and water, tends to shrink during drying. This shrinkage may be accompanied by cracking (Haxo 1982, Matrecon, Inc. 1980). Cement grouts may also shrink and this shrinkage can lead to the formation of microfissures (Littlejohn 1982). However, moist cured grout that remains moist will not shrink (Littlejohn 1982).

Cement mixtures are vulnerable to chemical attack because of their alkalinity, reactivity, and permeability. Penetration of fluids may be accompanied by chemical reaction of the fluid with cement constituents (ACI Committee 551 1979). Cement mixtures may deteriorate due to exposure to sulfates, chemical wastes, and organic acids (Tomlinson 1980). Further, cement hydration compounds may leach from the matrix and this can also cause deterioration (ACI Committee 515 1979).

Fluctuations in temperature during curing of cement mixtures may reduce the quality of the finished product. This is not normally a problem when using grouts in subsurface applications because ground temperatures are relatively stable.

Toxicity--

Cement grouts are essentially nontoxic. The basic components of the grout are Portland cement and water which are both nontoxic. Nonetheless, substances such as chemical polymers (acrylamide) may be added to the grout to modify its properties and these materials may be toxic.

Grout/Chemical Interactions

Cement materials are compatible with numerous substances. These are listed in Table 1. In general, cement materials such as grout are compatible with hydroxides, weak alkaline solutions, neutral salts, and heavy metals. Special cements, such as high alumina or supersulfate, are also resistant to acids. The compatibilities of specific chemicals with cement grout have not been documented, however, the compatibilities of chemicals with the cement materials listed in Table 1 should apply by analogy to cement grout.

A number of materials should not be used with cement grouts. These are listed in Table 2. These substances may interfere with the setting time of the cement or cause deterioration of the final product. Such deterioration may be caused by reaction with components of the cement resulting in leaching of the cement or disruption (cracking) of the grout matrix. For example, sulfates can react with tricalcium aluminate to form calcium sulfo-aluminate hydrate. This reaction causes swelling and cracking of the cement (Fung 1980, ACI Committee 515 1979). In addition, acids and some salt solutions can react with calcium hydroxide in hydrated Portland cement to form a solution of reaction products that can cause disintegration (ACI Committee 515 1979).

Areas of Application

Cement grouts have been used for many soil consolidation and water cutoff applications. Because of the relatively large particle size of cement, its use is restricted primarily to media of high porosity or permeability. Typically, cement grout cannot be used in fine grained soils with voids less than 0.1 mm wide because the large cement particles plug the soil matrix and prevent grout penetration (Bowen 1981).

Cement grout may be applied to fractured rock that has voids of sufficient size to ensure penetration of the grout. It may also be used for underpinning and construction of a variety of structures (Bowen 1981, Kirk-Othmer 1979). Type I Portland cement may be used for materials with large voids. Resin gypsum cements are used by the oil well cementing industry for rapid water seal-off applications. These cements set within 30 to 90 minutes (Bowen 1981).

Various materials may be added to cement grouts to improve their applicability. For example, a grout suitable for use in coarse soils may be prepared by adding sand to Portland cement and water (Bowen 1981). Bentonite may be added to improve the penetration of cement grouts in coarse grained soils (Soletanche [no date]).

Some specific applications of cement grouts and concrete are:

- Soil cement (Portland cement, water, soil) as a liner for hazardous waste landfills
- Cement stabilization of hazardous wastes

TABLE 1. MATERIALS COMPATIBLE WITH CEMENT

TYPE OF CEMENT	COMPOUND
Cement mortar (Portland, Portland/slag)	NaOH, KOH, $Mg(OH)_2$, $Ca(OH)_2$ Hypochlorite (Na, Ca) Other neutral salts except sulfates
Cement mortar (calcium aluminate)	Sulfates (Na, K, Ca, Mg) Other neutral salts $Ca(OH)_2$, MgOH Dilute sulfuric acid (pH 4-7)
Soil cement	Alkali (moderate amount) Organic matter (moderate amount) Inorganic salts (moderate amount) Oils
Concrete	Water Petroleum oil (with/without aromatics) Domestic sewage Strong oxidizers (nitrates, chlorates) Insoluble sulfates Heavy metals Common neutral salts (carbonates, nitrates, fluorides, silicates, some chlorides) Lime water Weak alkaline solutions Petroleum products (no fatty oil, acids) Hydroxides (<10%)
High alumina cement	Acids (as low as pH 3.5)
Supersulfate cement	Acids (as low as pH 3.5)

Source: ASTM 1982, Matrecon, Inc. 1980, Fung 1980, Tomlinson 1980, Malone, Jones, and Larson 1980, ACI Committee 515 1979.

TABLE 2. MATERIALS INCOMPATIBLE WITH CEMENT

TYPE OF CEMENT	COMPOUND
Cement mortar (Portland, Portland/slag)	Sulfates (Na, K, Ca, Mg) Dilute H_2SO_4 (pH 4-7) Other dilute acids/acid salts (pH 4-7)
Cement mortar (calcium aluminate)	KOH, NaOH Other dilute acids/acid salts (pH 4-7)* Hypochlorite (Na, Ca)*
Soil cements	Organic soils (>1-2% organic material) Sulfates Excess salt HNO_3 Highly ionic materials Strong acids Strong bases
Concrete	Animal oils Polyhydroxy organic compounds Salt solutions Mild acids Oxidizing acids Sulfates (Mg, Na, ammonium) Organic acids Halides Organic solvents and oil Organic materials Metal salts (Mn, Cu, Pb, Sb, Zn) Mineral acids
High alumina cement	Strong alkali

*Questionable

Source: ASTM 1982, Ingles and Metcalf 1973, Matrecon, Inc. 1980, Haxo 1980, Fung 1980, Tomlinson 1980, Malone, Jones, and Larson 1980, Thompson, Malone, and Jones 1980, ACI Committee 515 1979.

- Waterstop applications in dam construction.

PROPERTIES OF CLAY GROUTS

Clays have been widely used as grouts and in mixtures of grout materials. In general, coarse sands and gravels are initially grouted using clay or clay-cement grout because these grouts are relatively inexpensive (Guertin and McTigue 1982). Only certain types of clay minerals, possess the physical and chemical characteristics favorable for use in grouting. The important clay characteristics include the ability to swell in the presence of water and formation of a gel structure at low solution concentrations. Native clays can be utilized if they possess the necessary physical properties.

Although many clay minerals display one or both of the necessary properties to some degree, sodium montmorillonite is best. This mineral swells up to 15 times its volume when wetted, while most other clays merely double their volume (Grim 1968). In addition, sodium montmorillonite is highly thixotropic.

Chemical Composition and Reaction Theory

A source of sodium montmorillonite is bentonite, which is derived from the weathering of volcanic dust and ash deposits (Bowen 1981). Bentonites are composed primarily of the clay minerals sodium and calcium montmorillonite with about 10 percent impurities, such as iron oxides and native sediments (Boyes 1975, Grim 1968).

Montmorillonite clay is composed of three distinct layers. The outer layers are a tetrahedral arrangement of silicon and oxygen molecules with some of the silicon replaced by aluminum. Sandwiched between these two layers is a layer of aluminum atoms surrounded by six hydroxyls or oxygen atoms in an octahedral configuration. Some of the aluminum atoms in this layer have been replaced by magnesium. Because of the substitutions within the three layers, unsatisfied bonds exist within the crystalline structure. This results in a high net negative charge. To satisfy this charge, cations, such as sodium and calcium are adsorbed on the internal and external surfaces of the clay crystal. These cations cause the swelling of the montmorillonite as they adsorb water molecules, thus expanding the lattice layers (Brady 1974). Because there are limited quantities of natural sodium bentonites, some areas are forced to use specially treated calcium bentonites instead. This occurs most frequently in Europe. These calcium bentonites are exposed to sodium-containing materials such as sodium hydroxide to force some of the calcium ions off of the exchange complex of the montmorillonite and then replace them with sodium ions (Grim 1968). Sodium carbonate, which is less expensive and more effective than sodium hydroxide, is also used on some bentonites. As long as there is less than 30 percent calcium and at least 50 percent sodium on the exchange complex of the montmorillonite, the material will act essentially like a sodium montmorillonite (Grim 1968).

When hydrated bentonite particles are placed in suspension, they exhibit the property of thixotropic gelation, a property common to many colloidal systems (Tallard and Caron 1977b). Thixotrophy is the ability to form a gel structure in the suspension. When this structure is formed, the viscosity of the suspension becomes dependent on the rate of shear that is being applied to the system. If a low shear is applied, the viscosity will increase and a gel will form. If the rate of shear is high, as when the mixture is disturbed, the suspension will become liquid, and can be easily pumped (Tallard and Caron 1977b). This property allows a bentonite slurry to be kept in a liquid state through mixing until it is injected into the ground, where it will set into a weak gel upon the cessation of agitation (Leonard and Dempsey 1963). Since the thixotropic reaction is totally reversible, the bentonite will return to a fluid state if disturbed again (Xanthakos 1979).

Sodium montmorillonite is a great deal more thixotropic than are most clays. One indirect method of measuring thixotropy is by measuring the amount of clay needed to produce a clay-water slurry of a given viscosity. When using sodium montmorillonite, from 5 to 12 percent clay in water is needed to produce a 15 centiPoise (cP) slurry. If kaolinitic or illinitic native clays are used, from 25 to 36 percent clay is required to produced a slurry of the same viscosity (Grim and Guven 1978).

Bentonite Grout Properties

An initial viscosity of a bentonite suspension is usually set at 15 cP ± 5 cP. This ensures optimum injectability. Above this range, the suspension is too viscous and injectability drops sharply; below this range there is a risk of the bentonite settling out of suspension (Tallard and Caron 1977b). Because of the varied properties of available bentonites, the quantity necessary to reach this viscosity will range from 35 to 95 kg of bentonite per cubic meter of water (Tallard and Caron 1977b). This corresponds to between 5 and 12 percent bentonite and 88 to 92 percent water (Case 1982). The use of silicates as rigidifying agents in bentonite grouts allows less bentonite to be used and thus a lower viscosity is obtained. In one formulation, an initial viscosity of 3 to 4 cP is obtained (Tallard and Caron 1977b).

The setting time of bentonite grouts containing only clay is difficult to regulate since no setting agent is used (Tallard and Caron 1977b). The grout will start to set as soon as the injection pressures is decreased due to the formation of a gel structure within the soil pores. Once this process starts, the viscosity and the gel strength will increase with time. The final strength of the gel will depend on the setting time, colloid concentration, and composition of the suspending fluid (Xanthakos 1979). The final strength obtained, though, is very low compared to the strength of cement and other grouts (Tallard and Caron 1977b). If silicates are used as rigidifying agents, the set time of the grout can be controlled from a few minutes to five hours (Bowen 1981).

The shear strength of a bentonite gel is very low, thus, it cannot withstand steep hydraulic gradients unless filler materials are added.

Cement or chemical additives, such as silicates, can be used to increase the strength of the final gel (Greenwood and Raffle 1963). In clay-cement mixtures, the gelling ability of the bentonite can assist in stabilizing the cement. Chemicals, such as sodium silicate or acrylic resins, can also be added to bentonite to increase the rigidity of the gel (Bowen 1981, Tallard and Caron 1977b).

Because of bentonite's slow set time and low strength, it can be susceptible to wash out or erosion under water pressure (Tallard and Caron 1977b, Greenwood and Raffle 1963). In soils of high permeability, 10^{-1} cm/sec, water gradients of only 3 to 4 units can remove bentonite immediately after injection (Greenwood and Raffle 1963). This is much more likely to occur in coarse textured materials, such as open gravels where the grout must fill large open areas. In finer textured geologic units, wash-out is much less likely, particularly if filler materials are added to the bentonite grout. The filler will act to block the pore spaces, thus allowing the bentonite to set.

The basic ingredient in this type of grout, bentonite, is essentially nontoxic. The toxicity of most of the additives, such as sodium silicate, are also low, though gelling agents used to gel the sodium silicate could pose a risk (Tallard and Caron 1977b). These are discussed in more detail in the section on silicates.

Grout/Chemical Interactions

The presence of organic or inorganic compounds in the groundwater can have a detrimental effect on the ability of grout cut-off walls to contain pollutants. These chemicals can affect the physical/chemical properties of the bentonite used in construction of the wall. This can result in flocculation of the bentonite, reduced swelling of the bentonite, or the destruction of the bentonite mineral structure.

If the bentonite is injected into groundwater which contains high concentrations of electrolytes, such as sodium, calcium, and heavy metals, the bentonite could flocculate. This will result in particles that can exceed 10 microns in diameter, thus hampering the grout's ability to penetrate into the soil structure (Tallard and Caron 1977b, Matrecon, Inc. 1980, Alther 1981b).

Various organic and inorganic compounds can increase or decrease the amount of swelling that bentonite particles have undergone (Alther 1981b). This can lead to increased permeability of the in-place grout wall possibly resulting in breaching of the wall. For example, a decrease in the amount that hydrated bentonite has swelled increases the amount of pore space, thus increasing the permeability of the wall. All of the mechanisms that cause bentonite clay particles to shrink or swell will affect the quantity of water contained within the interspatial layers of the clay structure. Inorganic salts such as calcium can reduce the effective use of double layer of partially bound water surrounding the hydrated bentonite, thus reducing the effective size of the clay particles (D'Appolonia and Ryan 1979). Upon dissociation, organic bases can be sorbed into the internal surfaces of clay particles thus affecting the interlayer spacings (Anderson and Brown 1981). Neutral-nonpolar and neutral polar compounds can replace the water contained in the clay particle interlayers, thus affecting the size of the bentonite particle (Anderson and Brown 1981). For example, one study (Anderson, Brown, and Green 1982) found that undiluted acetone, a neutral polar compound, caused a significant increase in the permeability of four types of clay as shown in Table 3. A 1,000-fold permeability increase was found for one type of montmorillonite. After contact with the acetone, the clays showed extensive shrinkage and cracking. Such clay shrinkage is usually associated with dehydration, indicating that acetone extracted water from the soil surfaces. This study also showed that clays exposed to concentrated xylene, a neutral non-polar compound, had a 100-fold increase in permeability. The xylene treated clays showed signs of structural changes that led to the permeability increase (Anderson, Brown, and Green 1982). It should be noted that most laboratory studies on bentonite-chemical compatibilities subject the bentonite samples to much higher concentrations of chemicals than are common in actual site conditions. Additionally, laboratory test procedures have not been standardized nor have many of the results been verified. For this reason, the results should be used merely as indications of the general effects of the chemicals on the bentonite rather than as exact predictions of the overall effects.

Strong organic and inorganic acids and bases can dissolve or alter the bentonite leading to large permeability increases (D'Appolonia and Ryan 1979, Alther 1981b). Aluminum and silica, two of the major components of bentonite, are readily dissolved by strong acids or bases, respectively (D'Appolonia and Ryan 1979, Matrecon, Inc. 1980). For example, when four types of clays were exposed to acetic acid, significant soil piping occurred due to the dissolution of the soil components as shown in Table 3 (Anderson, Brown, and Green 1982). This led to a increase in permeability in most of the clay types, though strong bases usually produce a greater increase in permeability than acids (D'Appolonia and Ryan 1979).

Recent laboratory studies have shown the effects of a variety of inorganic and inorganic compounds on soil-bentonite mixtures containing one percent bentonite (D'Appolonia and Ryan 1979, D'Appolonia 1980a). Table 4 illustrates the results of these studies. As can be seen, strong acids and bases will increase the mixture's permeability through dissolution. Undiluted alcohol will increase the permeability, probably through extracting water from the clay interlayers, thus reducing the amount of particle swelling. High concentrations of calcium will also increase permeability, probably by exchanging with the sodium ions on the bentonite, thus reducing the amount of particle swelling.

The surface of bentonite clay particles can be chemically modified to increase the bentonites' resistance to the detrimental effects of various types of chemicals. These bentonites are specially treated with proprietary

TABLE 3. EFFECT ON PERMEABILITY OF SEVERAL UNDILUTED ORGANIC CHEMICALS ON SELECTED CLAYS

CHEMICAL	SODIUM-SATURATED MONTMORILLONITE		CALCIUM-SATURATED MONTMORILLONITE		KAOLINITE		ILLITE	
	Effect on Permeability	Magnitude of. Change	Effect on Permeability	Magnitude of Change	Effect on Permeability	Magnitude of Change	Effect on Permeability	Magnitude of Change
Acetic acid	I	<10	D	10-100	D	1,000	D	<10
Aniline	I	100	I	<10	I	10	I	10-100
Ethylene glycol	I	100	I	<10	D	10	D	<10
Acetone	I	1,000	I	<10	I	10-100	I	100
Methanol	I	1,000	I	100	I	10-100	I	100
Xylene	I	1,000	I	10-100	I	100	I	1000

I: Increase
D: Decrease

Source: Anderson, Brown, and Green 1982

TABLE 4. SOIL/BENTONITE PERMEABILITY INCREASES DUE TO LEACHING WITH VARIOUS POLLUTANTS

Pollutant	Backfill[+]
Ca^{++} or Mg^{++} @ 1,000 ppm	N
Ca^{++} or Mg^{++} @ 10,000 ppm	M
NH_4NO_3 @ 10,000 ppm	M
Acid (pH>1)	N
Strong acid (pH<1)	M/H*
Base (pH<11)	N/M
Strong base (pH>11)	M/H*
HCl (1%)	N
H_2SO_4 (1%)	N
HCl (5%)	M/H*
NaOH (1%)	M
CaOH (1%)	M
NaOH (5%)	M/H*
Benzene	N
Phenol solution	N
Sea water	N/M
Brine (SG=1.2)	M
Acid mine drainage ($FeSO_4$, pH 3)	N
Lignin (in Ca^{++} solution)	N
Organic residues from pesticide manufacture	N
Alcohol	M/H

N - No significant effect; permeability increase by about a factor of 2 or less at steady state.
M - Moderate effect; permeability increase by factor of 2 to 5 at steady state.
H - Permeability increase by factor of 5 to 10.
* - Significant dissolution likely.
+ - Silty or clayey sand, 30 to 40% fines.
Source: D'Appolonia 1980a, D'Appolonia and Ryan 1979.

compounds consisting of organic and inorganic polymers.* This type of bentonite was developed for use in the construction of liners for lagoons and landfills and there were no references found as to its current use in grouting.

Areas of Application

Bentonite grouts alone can be used as waterproofing in coarse sands with an hydraulic conductivity of more than 10^{-1} cm/sec. Bentonite-chemical grouts can be used on medium to fine sands with an hydraulic conductivity between 10^{-1} cm/sec and 10^{-3} cm/sec. Both of these grout types can also be utilized to seal small rock fissures (Guertin and McTigue 1982). All bentonite grouts can only be used for waterproofing due to their low gel strength (Tallard and Caron 1977b).

PROPERTIES OF CEMENT-BENTONITE GROUTS

A suspension of bentonite and Portland cement can be used for grouting in situations that require both low permeability and resistance to moderately high hydraulic pressure. In general, the mixture contains about 6 percent bentonite, 18 percent cement, and 76 percent water (Jefferis 1981).

Chemical Composition and Reaction Theory

The chemical composition of both the Portland cement and the bentonite used in cement-bentonite grouts was described earlier in this section. The reactions that occur during mixing and hardening of these grouts and the procedures used during mixing are described below.

To obtain a satisfactory cement bentonite grout, the bentonite must be carefully mixed with water and allowed to fully hydrate (i.e., reach a constant viscosity) prior to the addition of the cement. This is because the calcium in the cement adversely affects the properties of the sodium montmorillonite in the bentonite by replacing the exchangeable sodium, thus reducing the radius of the bentonite particles and causing partial flocculation (Jefferis 1981). The montmorillonite would then fail to swell properly and would lose its thixotropic properties (Case 1982). If the bentonite is allowed to hydrate fully first, however, these effects are minimized.

When the bentonite suspension and the cement are mixed, flash stiffening occurs. If the mixture is rapidly and continuously agitated, the initial stiffening softens and a pasty suspension is formed (Jefferis 1981). This grout remains workable for several hours, after which set up begins (Case 1982). If agitated, the grout will remain workable longer but it may lose its ability to set if agitated longer than several days (Jefferis 1981).

---

*Hentz, D.A., Federal Bentonite, Belle Fourche, SD. Verbal communication with G. Hunt, JRB Associates, June 3, 1982.

Cement-Bentonite Grout Properties

Unlike bentonite grouts, cement-bentonite grouts have the ability to withstand significant hydraulic gradients, however cement bentonite grouts are more permeable than are bentonite grouts. Once a properly formulated cement-bentonite grout has cured, it is expected to have a strength on the order of 15 to 55 psi (Case 1982; Millet and Perez 1981). Cement-bentonite mixtures have been used to withstand with hydraulic gradients well in excess of 200 units without damage (Jefferis 1981).

Grout/Chemical Interactions

The compatibility between cement-bentonite grouts and various chemical constituents can be considered to be a combination of the individual compatibilities and incompatibilities of cement and bentonite. The chemicals that degrade bentonite in a bentonite grout can be expected to degrade the exposed bentonite in a bentonite-cement grout. Similarly, the cement will be attacked by cement-degrading chemicals, only the damage is likely to be less substantial due to the protective influence of the bentonite. Chemicals that enhance or disrupt cement grouts were listed in Tables 1 and 2, respectively. Chemicals that affect the permeability of water barriers composed of bentonite were listed in Table 3.

Areas of Application

Cement-bentonite grouts can be emplaced both horizontally and vertically to inhibit subsurface water movement. In addition, the material can be used to partially stabilize soil materials during some types of excavation activities.

An example of the use of cement-bentonite grout is in a subway station excavation for a that needed dewatering. To accomplish this, a cement-bentonite slurry cut-off wall was planned. The wall planned, however, did not extend to a sufficient depth to completely divert water movement. For this reason, cement-bentonite grout was injected vertically into the fairly granular soil and rock material below the base of the wall. The floor of the proposed subway station was also susceptible to seepage. To prevent this, area grouting was conducted using additional cement-bentonite grout (Guertin and McTigue 1982).

PROPERTIES OF SILICATE GROUTS

Alkali silicates are the most widely used class of grouts in the chemical grout category. Sodium, potassium, and lithium silicates are used with sodium silicates being used most often. Chemical grouts (silicates and organic polymers) constitute less than 5 percent of the grouting in the United States. In Europe, these grouts represent almost 50 percent of the grouts used (Kirk-Othmer 1979).

As early as 1886, a German patent was assigned for use of silica gel to fill voids (Tallard and Caron 1977a). One of the earliest uses of silicates as grouts was in 1915 when silicate was used in conjunction with cement grout. Soon after, the Joosten two-shot method (sodium silicate and calcium chloride) was developed and used to grout deep foundations. In addition to their use as grout, sodium silicates may be used as additives to other grouts such as Portland cement to improve strength and durability (Hurley and Thornburn 1971).

Chemical Composition and Reaction Theory

Silicate grouts consist of alkali silicates, water, and a gelling or setting agent. Typically, sodium silicate is used in the grout, however, potassium silicate may be substituted. The gelling or setting agent varies depending on the desired properties of the gel. In general, acids, acid-forming compounds, polyvalent cations, and some organics, may be used as setting or gelling agents (Kirk-Othmer 1979, Hurley and Thornburn 1971). The grout may also include an accelerator. Accelerators consist of chlorides, aluminates, or bicarbonates (Johnson 1979). Other substances, such as organic esters, may be added to delay gelling time (Bowen 1981).

Grout materials vary with the grouting method to be used. In the Joosten method, calcium chloride is the most commonly used setting agent. Other salts (magnesium chloride, aluminum sulfate) and gel-forming gases (carbon dioxide) may also be used. The Siroc (one shot) method typically uses formamide although other substances (bicarbonate, sodium aluminate, calcium chloride, dilute hydrochloric acid, copper sulfate) may be used (Bowen 1981, Sommerer and Kitchens 1980, Office of the Chief of Engineers 1973). Sometimes the Siroc method uses two reactants with the second reactant serving as an accelerator (Office of the Chief of Engineers 1973). In Europe, most silicate grouts use only organic reactants (Karol 1982a). It should be noted that each company may use different reactants, thus the grouting compositions vary considerably and are often proprietary (Herndon and Lenahan 1976a).

The gelling process is a two step reaction that generally involves neutralization of the basic silicate and involves a lowering of the pH of the silicate. A decrease in the electric charge on the silicate ions followed by polymerization of silicates with the reagent, forms a three dimensional network of chains of silicate micelles (Sommerer and Kitchens 1980, Kirk-Othmer 1979, Hurley and Thornburn 1971). The network is established through hydrogen bonding and silicon-oxygen bonding (Sommerer and Kitchens 1980, Hurley and Thornburn 1971). Where metal salts are used, a colloidal mixture is achieved through precipitation of a metal silicate. The mechanism for formation of such an amorphous precipitate is due to either the adsorption of metal ions on gelatinous silica or the mutual coagulation of colloidal metal hydroxide (positive charge) and colloidal silica (negative charge) (Hurley and Thornburn 1971).

Silicate Grout Properties

The viscosity of sodium silicate grouts varies from 1.5 to 50 cP and may be as high as 260 cP (Sommerer and Kitchens 1980, Tallard and Caron 1977a). Silicate grouts used in the Joosten method have a high viscosity while other silicate grouts have a moderate viscosity (Karol 1982b). The viscosity of the grout depends on the ratio of SiO_2 to Na_2O and the water content. The higher the ratio of silica to sodium, the lower the viscosity. The water content will also control the grouts viscosity. The higher the water content the lower the viscosity. For waterproofing gels a dilution of 70 to 90 percent is commonly used (Tallard and Caron 1977a and b).

The set time of the silicate grouts varies from less than a minute to several hours (2 to 10). The Joosten method has almost instantaneous set while the Siroc method is more variable (Sommerer and Kitchens 1980, Kirk-Othmer 1979, Tallard and Caron 1977a, Tallard and Caron 1977b). Factors affecting the set time include silicate concentration, setting agent concentration, and temperature. Increasing any of these three factors will decrease the set time (Tallard and Caron 1977a). The accelerator concentration may also be varied to control set time. In either case, the set time is controlled by the rate of acid formation because this controls the neutralization or polymerization process (Karol 1982a). Soil conditions can also affect the set time with acid soils reducing gel time and alkaline soils reducing or preventing gel formation (Office of the Chief of Engineers 1973).

Tallard and Caron (1977a) report that silicate grout is quite durable and silicate treated areas have not lost their watertightness and strength characteristics after some time. However, long-term strength and impermeability are of concern because silicate grouts are subject to deterioration via syneresis (water expulsion), shrinkage (dessication), and solution erosion by groundwater (Hurley and Thornburn 1971). Silica gels may lose as much as 20 to 60 percent of their water (by weight) within two months due to synersis (Hurley and Thornburn 1971). In syneresis, salt-charged water is expelled through the polycondensation of silicic acid (Karol 1982a). Shorter gel times mitigate this problem and syneresis has less effect in fine soils (Karol 1982a). Further, silica gels may shrink and crack upon aging (Hurley and Thornburn 1971). In an excess of water, leaching may occur. This will dissolve the silica gel's soluble salts and the gel may revert to soluble material (Kirk-Othmer 1979, Tallard and Caron 1977b). Gels formed from more viscous grout mixes tend to shrink excessively. This shrinkage process can continue for some time and can lead to disintegration of the gel (Williams 1966). In addition, any unreacted sodium in the grout will pass into the cure water and may attack the polysilicic acid (grout matrix) (Tallard and Caron 1977b).

Sodium silicate grouts are essentially nontoxic. The set grout has a relatively low toxicity (oral) having an LD_{50} of 15 g/kg in laboratory animals, while sodium silicate has an LD_{50} (oral) of 1,100 mg/kg. Amides frequently used in formulating the grout are skin irritants (Tallard and Caron 1977b). Other organic substances, such as formamide, are toxic, possibly carcinogenic, and require special precautions when preparing and injecting the grout (Karol 1982a, Kirk-Othmer 1979, Tallard and Caron 1977a). Heavy metal salts, which may be used as gelling agents, are also toxic and have the potential to be leached from the gel. In addition, sodium salts may be expelled from the grout and under certain circumstances they may be an environmental hazard (Karol 1982a).

Grout/Chemical Interactions

Silicate grouts, when set, are resistant to moderate amounts of acids or alkali (Kirk-Othmer 1979). These grouts are also resistant to high concentrations of chromic, nitric, and sulfuric acid (Boova 1977). Organic esters have little effect on silicate grout (Bowen 1981). Silicate mortar is similar to silicate grout but also contains fillers such as silica, quartz, or ganister. This mortar is resistant to most acids (except hydrofluoric acid) as well as neutral salt solutions (ASTM 1982).

Gelation of silicate grouts occurs through the action of acids or acid salts. Hurley and Thornburn (1971) and Karol (1982a) report that the setting time of silicate grouts is significantly decreased in the presence of soils or groundwater with an appreciable salt content. These effects may be mitigated by using groundwater to mix the grout. Acidic soils may also decrease the gel time (Karol 1982a).

Silicate grouts are not compatible with a number of materials that may be found in hazardous waste sites. Gel time and grout strength may be affected by large amounts of acid or alkali (Kirk-Othmer 1979). Additionally, organic materials and high concentrations of some metals will slow the setting time (Malone, Jones, and Larson 1980).

Areas of Application

Silicate grouts are used for both soil consolidation and waterproofing applications. These grouts are suitable for blocking water migration in soils with a permeability of less than 10^{-2} cm/sec. Silicate grouts are not suitable for open fissures or highly permeable materials (due to syneresis) unless they are preceded by cement grouting (Karol 1982a, Sommerer and Kitchens 1980). The Joosten method has been used for both fine sands and gravels while the Siroc method has been used to waterproof sands (Kirk-Othmer 1979, Tallard and Caron 1977a). Tests by the U.S. Army Corps of Engineers, Waterways Experiment Station, however, found silicate grouts to be ineffective in waterproofing fine grained soils (Hurley and Thornburn 1971). Currently, silicate-based grout is under study for use in controlling hazardous chemical spills (Sommerer and Kitchens 1980)

PROPERTIES OF ORGANIC POLYMER GROUTS

Organic polymer grouts represent only a small fraction of the grouts in use. These grouts consist of organic chemicals (monomers) that polymerize and crosslink to form an insoluble gel. This section addresses acrylamide, phenolic, urethane, urea-formaldehyde, epoxy, and polyester grouts, and their properties.

Properties of Acrylamide Grouts

Acrylamide grouts have been in use for 30 years. These grouts were the first of the organic chemical polymer grouts to be developed. Acrylamide grouts have the largest use among the organic polymer grouts. They are the second most widely used chemical grout (Karol 1982a). They may be used alone or in combination with other grouts such as silicates, bitumens, clay, or cement (Tallard and Caron 1977a).

AM-9 was the first acrylamide grout developed; it was removed from the market in 1978 because of the problems involved with the toxicity of the accelerator in AM-9 (Karol 1982a). There are only a few acrylamide or acrylamide-based grout products available and most of them are imported. These grouts include acrylates, polyacrylamides, and acrylamide derivatives. Some grouts, such as Rocagil 1295, are not used in the United States (Karol 1982a). Although AM-9 was removed from the market, it has been used as recently as 1980 in water cut-off applications (Berry 1982). A number of acrylamide grouts that were copies of AM-9 have been imported and marketed after AM-9's removal (Karol 1982). AM-9 is probably the most studied of the acrylamide grouts. Because of the similarity of the materials and the reaction mechanisms, much of the AM-9 data is valid for other acrylamide grouts (Karol 1982a). Thus, the data are included in the following discussions of acrylamide grout properties.

Chemical Composition and Reaction Theory--

Acrylamide grouts consist of a base material (typically a monomer or mixture of monomers), a crosslinking agent, an initiator or catalyst, and an accelerator or activator. Persulfates or peroxides, typically ammonium persulfate, are used as the initiator. Accelerators/activators include dimethylaminopropionitrile, diethylaminopropionitrile, or triethanolamine (Tallard and Caron 1977a). The substances used vary with the particular product. Table 5 summarizes the components of the major acrylamide grouts. Two of these grouts, AC-400 and Injectite-80, do not utilize acrylamide but instead use a related compound or a pre-polymer. These substances have a lower toxicity. AM-9, while discontinued, is included because of the presence of similar products on the market.

Polymerization occurs through a reduction/oxidation (redox) reaction. Acrylamide contains two reactive sites: a double bond and an amide. Reaction at the double bond creates a polymerization similar to vinyl compounds. The resulting linear polymers are soluble in water. To obtain an insoluble polymer, crosslinking or reticulating agents are used to form bridges between the linear polymers. This is accomplished at the amide group through a condensation reaction with aldehydes (formaldehyde, glyoxal, etc.). The degree of crosslinking will determine the polymer properties (Tallard and Caron 1977a). During polymerization, water becomes trapped in the gel matrix (Karol 1982a, Berry 1982).

TABLE 5. COMPONENTS OF ACRYLAMIDE GROUTS

PRODUCT	BASE MATERIAL	CROSS-LINKING AGENT	INITIATOR/ CATALYST	ACCELERATOR/ ACTIVATOR	REFERENCES
AM-9	Acrylamide	Methylenebis-acrylamide	Ammonium persulfate	Dimethylamino-propionitrile	Bowen 1981 Tallard and Caron 1977a
Q-Seal	Acrylamide	N,N'-methylenebis-acrylamide	Ammonium persulfate	Triethanolamine	Cues, Inc. 1982
AV-100	Acrylamide	unspecified	Ammonium persulfate	Triethanolamine	Avanti International, 1981
AC-400	Acrylate	Methylenebis-acrylamide	Ammonium persulfate	Triethanolamine	Clarke 1982 Geochemical Corporation 1982
Injectite® -80	Polyacrylamide	Glyoxal	Calcium hypo-chlorite	Trisodium phosphate	Berry 1982 Jacques 1981

Additional substances may be added to control the grout. Gel time may be controlled through the addition of a reaction inhibitor, typically potassium ferricyanide (Karol 1982a, Tallard and Caron 1977a). Buffers may be required to maintain the pH of the grout solution around 8. Disodium phosphate is added when no activator is used (Office of the Chief of Engineers 1973).

Acrylamide Grout Properties--

Most of the acrylamide grouts (pre-gel) have a low viscosity; less than 2 cP. Their viscosity is approximately that of water (Karol 1982a, Geochemical Corporation 1982, Cues, Inc. 1982, Avanti International 1982, Tallard and Caron 1977b, Herndon and Lenahan 1976b). Injectite^{R}-80 is more viscous and at normal grout concentrations (10%), has a viscosity of 50 cP (Berry 1982). Addition of polymerization agents or cement will increase the viscosity (Avanti International 1982, Tallard and Caron 1977b). Overall, the viscosity will remain constant until gelation occurs (Karol 1982a, Avanti International 1982).

The set time, or gelation, can vary from a few seconds to several hours (12 to 48) (Karol 1982a, Cues, Inc. 1982, Tallard and Caron 1977a, Office of the Chief of Engineers 1973). The factors primarily controlling set time are reaction inhibitors and the proportions of catalyst and activator (Karol 1982a, Kirk-Othmer 1979, Tallard and Caron 1977a). In general, the set time is lengthened by addition of inhibitors (potassium ferricyanide) or by decreasing the amount of catalyst in the grout mixture (Karol 1982a, Tallard and Caron 1977a). An acidic grout solution or acidic grouting conditions (groundwater or earth material) can also lengthen the set time and may prevent gelation (Office of the Chief of Engineers 1973). The set time may be shortened through the action of metals, triethanolamine, or ammonium persulfate; increasing the pH; or by increasing the dry matter in the grout (Clarke 1982, Avanti International 1982, Tallard and Caron 1977a, Office of the Chief of Engineers 1973).

Once the grout is set, it is chemically stable and is not subject to slow deterioration or syneresis (Karol 1982a, Berry 1982, Avanti International 1982, Tallard and Caron 1977a). A small portion of the grout remains hydrolyzable even after setting and under certain conditions it may rehydrolyze and become soluble (Tallard and Caron 1977a). Eventually, some salts, unreacted material, and hydrolysis products may leach out (Karol, 1982a, Tallard and Caron 1977a). Further, acrylamide gels are approximately 90 percent water and they may shrink or swell due to exposure to water fluctuations or subsurface forces acting on the gel (Karol 1982a, Kirk-Othmer 1979). After shrinkage, the gel can regain its original volume. Shrinkage cracks may seal but not heal, i.e., the crosslinkages of the molecular chains do not reform, resulting in greater permeability and less strength (Karol 1982a). The permeability may thus increase due to shrinkage cracks. In addition, soluble salts may migrate through the water contained within the gel's polymeric structure (Karol 1982a).

All of the acrylamide grout formulations contain substances that are toxic and require special handling (Berry 1982, Geochemical Corporation 1982, Tallard and Caron 1977a). Acrylamide (solution or powder) is neurotoxic (Karol 1982a) and, unreacted, has an LD_{50} of 150 mg/kg (Berry 1982). Methylenebisacrylamide, a common crosslinking agent, has an LD_{50} of 390 mg/kg, but is not neurotoxic (Geochemical Corporation 1982). The gelled grouts, however, or polymerized acrylamides are reported to be nontoxic. Injectite^{R}-80 base material, a low molecular weight polyacrylamide, has an LD_{50} of 5,000 mg/kg, which is higher than common table salt (Berry 1982). AC-400, after gelation, also has an LD_{50} of 5,000 mg/kg (Geochemical Corporation 1982, Clarke 1982). It should be noted that if the polymerization process is not complete, unreacted toxic monomer or other substances can leach from the grout matrix and has caused problems in the past (Tallard and Caron 1977a).

Grout/Chemical Interactions--

Acrylamide grouts are resistant to the dilute chemicals found in sewer systems. Normal groundwater conditions (dilute acids, alkali, salts) will have little effect, particularly if groundwater is used to mix the grout (Clarke 1982, Avanti International 1982, Kirk-Othmer 1979). Acrylamide grouts are impermeable to gases and hydrocarbon solvents such as kerosene, toluene, heptane, and dilute hydrochloric acid (2 percent) (Office of the Chief of Engineers 1972, Berry 1982). They are also unaffected by 10 percent solutions of alcohols, ketones, hydrocarbons, acids, and metal salts (Clarke 1982).

Salts and pH will affect the setting time of acrylamide grouts. (Caron 1963). Low pH conditions, (<6.5), can prevent acrylamide grouts from setting. Polymerization inhibitors such as sodium nitrates and metallic salts can also delay gelation (Avanti International 1982, Office of the Chief of Engineers 1973). Alkaline conditions or metal ions, such as iron, copper, zinc, or tin, can shorten the gelation time (Avanti International 1982, Tallard and Caron 1977a). Other gel time accelerators include hydrogen sulfide and soluble salts (NaCl, $CaCl_2$, sulfates, phosphates) (Karol 1982a, Office of the Chief of Engineers 1973).

The durability of acrylamide grout is affected by highly alkaline media which can promote saponification of the grout, particularly the monomer (Sommerer and Kitchens 1980, Tallard and Caron 1977a). This hydrolysis reaction will affect the performance of the grout (Tallard and Caron 1977a).

Herndon and Lenahan (1976b) report that sulfides affect acrylamide grout, but the effect is not specified. Strong or concentrated hydrating and dehydrating agents will have the greatest impact on acrylamide grouts. For example, acrylamide grouts will swell in the presence of sulfuric acid, sodium chloride, sodium sulfite, sodium hydroxide, and laundry detergent. Alcohols and glycols will cause the grout to shrink by drawing out the water (Berry 1982).

Areas of Application--

Acrylamide and acrylamide-based grouts have greater use in the United States than in Europe, where phenolic grouts find more use. Acrylic and polyacrylamide grouts are typically used in ground surface treatment, ground treatment for oil well drilling, and subsurface applications (waterproofing concrete structures). Acrylate grouts find greater use in ground surface treatment than soil injection, where acrylamide grouts are frequently used. Acrylamide applications include structural support and seepage control for mines, soil consolidation for foundations of structures and dams, and water control/soil consolidation for tunnels, wells, and mines (Tallard and Caron 1977a). Specific applications include grout curtains, stabilization of loose sand, shut-off of artesian flow, and control of water seepage in jointed and fissured rock (Office of the Chief of Engineers 1973). Based on AM-9 applications, acrylamide grouts may be used in a variety of soil materials such as fine gravel; coarse, medium, or fine sand; coarse silt; and clay soil (Herndon and Lenahan 1976b).

Properties of Phenolic Grouts

The use of phenolic resin grouts in underground and foundation construction began in the 1960's (Kirk-Othmer 1979, Tallard and Caron 1977a). These grouts may be used in fine soils and sands in a variety of waste control and ground treatment applications. Phenolic grouts however, are not widely used; when used, they are typically employed in conjunction with other grouts (Tallard and Caron 1977a).

Chemical Composition and Reaction Theory--

Phenolic grouts are commonly referred to as phenoplasts. They are polycondensates of phenols and aldehydes (Sommerer and Kitchens 1980, Tallard and Caron 1977a). A typical grout consists of a phenol, an aldehyde, water, and a catalyst. Formaldehyde is used almost exclusively as the aldehyde because of its high reactivity (Billmeyer 1971). The catalyst may be an acid or a base (Tallard and Caron 1977a, Billmeyer 1971). Since soil conditions are typically neutral or somewhat basic, an acid catalyst would preferentially react with soil materials rather than the grout (Tallard and Caron 1977a). Therefore, sodium hydroxide or other alkaline materials (hydroxides, carbonates, phosphates) are typically used as catalysts to provide an alkaline reaction medium and to control the pH (Karol 1982a, Tallard and Caron 1977a).

Not all phenols can react in an alkaline medium. Resorcinol and byproducts containing large amounts of resorcin (such as tannin extracts) can undergo alkaline reactions and these materials constitute the majority of the phenolic grouts (Karol 1982a, Tallard and Caron 1977a). Table 6 summarizes the major components of some of the commercial phenolic grouts.

Phenolic grouts may be mixed in a one or two solution system. The proportions of phenol, formaldehyde, and catalyst are fixed by reaction requirements so the only variable is the amount of water added (Tallard and Caron 1977a). Polymerization begins as soon as the solutions or grout components are mixed. In general, polyvalent cations from the alkali catalyst initiate and promote polymerization (Chung 1973). The polymerization (polycondensation) process results in the formation of a three dimensional network of polymer chains (phenol) that are joined and crosslinked by formaldehyde (Karol 1982a, Bowen 1981, Tallard and Caron 1977a). The

TABLE 6. PHENOL RESIN GROUT PRODUCTS

Product	Composition	References
Rocagil	Partially sulfonated tannin Formaldehyde	Sommerer and Kitchens 1980 Karol 1982a
Geoseal	Tannin Mimosa extract Phenolic precondensate Formaldehyde/paraformaldehyde Salts Catalyst (sodium hydroxide)	Bowen 1981 Chung 1973 Karol 1982a
Terranier	Low molecular weight polyphenolic polymers or lignosulfonate Catalyst (formaldehyde) Activator (modified metal salt--sodium dichromate)	Bowen 1981 Chung 1973 Karol 1982a

catalyst is also attached to the polymer resin and it may form secondary linkages within the resin network or bond with the soil. The resulting resin is insoluble and retains all constituent materials (Tallard and Caron 1977a).

Phenolic Grout Properties--

Phenolic grouts have low viscosity. Phenolic grouts made with resorcinol and formaldehyde have viscosities between 1.2 and 3 cP for normal field concentrations (Karol 1982a, Tallard and Caron 1977b). Commercial products consisting of tannin or polyphenols typically have a higher viscosity: Geoseal ranges from 2 to 12 cP; Terranier ranges from 4 to 10 cP; Rocagil ranges from 5 to 10 cP (Bowen 1981, Tallard and Caron 1977a, Tallard and Caron 1977b). The viscosity depends on the concentration of the grout (Tallard and Caron 1977a). As with acrylamides, resorcinol-formaldehyde grouts remain of constant viscosity until gelation occurs. With tannin-based grouts, the viscosity gradually increases (after the components are mixed) until set is achieved (Karol 1982a, Tallard and Caron 1977b).

The gel or set time of phenolic grouts may vary from several minutes to several hours (Bowen 1981). The gel time is primarily controlled by the diluteness of the grout with short gel times for concentrated grout solutions and long gel times for dilute solutions (Karol 1982a, Tallard and Caron 1977a). With very dilute solutions, gelation may never occur and the grout becomes unusable (Tallard and Caron 1977a). If all other factors remain constant, the choice of catalyst will affect the set time because different bases have different reactivities. Sodium hydroxide, the most common catalyst, provides approximately a 20 minute gel time as do some carbonates and calcium hydroxide. Other bases (hydroxides and carbonates) provide longer set times (Tallard and Caron 1977b).

The length of set time affects the strength of the grout, with short set times giving strong gels and long set times giving weak gels. Strong grouts are not critical to waterproofing, but short set times are often important (Karol 1982a). To decrease the set time, phenolic grouts may be combined with another grout, such as a silicate, that has a shorter set time. This other grout will set first and provide a "false set." The phenolic grout is retained in the grout matrix and sets at its normal rate. The final properties of the grout mixture are determined by the phenolic grout (Tallard and Caron 1977a).

Wet cured phenolic grouts (under the water table) are generally durable, however, there may be a slight weakening over time due to gradual swelling of the resin (Tallard and Caron 1977b). After setting is complete, the phenolic resin contains water that is not chemically bound in the matrix. Under drying conditions, this water can evaporate and the gel may shrink and crack (Sommerer and Kitchens 1980, Tallard and Caron 1977a, Tallard and Caron 1977b). Unlike acrylamides and silicates, this dehydration is irreversible and can lead to disintegration of the gel (Karol 1982a, Tallard and Caron 1977a).

Proper proportioning of phenol and formaldehyde in phenolic grout will produce a complete reaction and the resulting gel is relatively insoluble and inert (Tallard and Caron 1977a, Tallard and Caron 1977b). If the materials are not properly proportioned, excess materials may leach out of the resin. In either case, some of the catalyst may remain partially soluble and leach out of the matrix (Karol 1982a, Tallard and Caron 1977a, Tallard and Caron 1977b).

Phenolic grouts contain toxic and caustic materials which require special handling (Karol 1982a, Tallard and Caron 1977b). The toxicity of some of the grout components are summarized below (Tallard and Caron 1977b):

Chemical	Oral LD_{50}	Skin LD_{50}
Resorcin	301 mg/kg	2,050 mg/kg
Phenol	414 mg/kg	699 mg/kg
Formaldehyde	800 mg/kg	260 mg/kg

In handling these compounds, standard safety precautions as outlined in the handling procedures provided with the grout should be followed including the use of gloves, respirators, and protective garments. The hardened grout is essentially nontoxic and noncaustic (Bowen 1981). If the constituents are improperly proportioned however, excess (unreacted) material may leach from the matrix (Tallard and Caron 1977b).

Grout/Chemical Interactions--

Phenol-formaldehyde resins are resistant to organic solvents (Billmeyer 1971). Phenolic resin mortars are recommended for use with organic acids, wet gases (reducing), nonoxidizing and nonreducing gases, nonoxidizing mineral acids (except hydrofluoric acid), and highly concentrated sulfuric acid (>85%). These recommendations are based on immersion of the mortar in these compounds (ASTM 1982).

Phenolic resins are not resistant to alkaline substances (Boova 1977). Both strong acids and bases will attack phenol-formaldehyde resins (Billmeyer 1971). Phenolic resin mortars are not recommended for use with bleaches or wet gases (oxidizing), but are recommended for limited use with oxidizing mineral acids, inorganic alkali, and organic solvents (ASTM 1982).

Areas of Application--

Phenolic grouts are used in soils of low permeability such as fine gravel and coarse, medium, and fine sand. (Sommerer and Kitchens 1980, Herndon and Lenahan 1976b). These grouts have been used to stop leaks in railway tunnels and for ground surface treatment (Flatau, Brockett, and Brown 1972, Tallard and Caron 1977a). Phenolic grouts find their greatest use in combination with silicate grouts in treating fine sands and silts (Tallard and Caron 1977a).

Different phenolic grout products have been formulated to meet different needs. Geoseal MQ-4 was designed for resistance to saline groundwater while Geoseal MQ-14 was designed for treating low permeability materials. In addition, Terranier C was designed for grouting silts (Bowen 1981).

Properties of Urethane Grouts

Urethane grouts are the second most commonly used organic polymer grouts (Jacques 1981). Urethane grouts were developed in Germany for consolidation applications, and are now used in Europe, South Africa, Australia, and Japan*, (Sommerer and Kitchens 1980). These grouts are used for waterproofing and soil applications, and can penetrate finely fissured material.

Chemical Composition and Reaction Theory--

Urethane, or polyurethane, grout consists primarily of a polyisocyanate and a polyol or other hydroxy compounds such as polyethers, polyesters, or glycols (Karol 1982a, Vinson and Mitchell 1972). A diisocyanate is often used as well (Vinson and Mitchell 1972). RokLok®, a polyurethane grout, consists of polymethylene polyphenyl isocyanate (containing diphenylmethane diisocyanate) and poly(oxyalkylene) polyether polyol resin (Mobay Chemical Corporation 1982). Other substances may be added as catalysts, surfactants, dilution agents, plasticizers, and stabilizers. These materials control the reaction of the grout and its properties before and after setting.

Urethane grouts set through a multistep polymerization process. The initial reaction occurs between excess isocyanate and the polyol compound to form a polyurethane prepolymer (Jiacai et al. 1982, Karol 1982a). To complete the reaction sequence, the prepolymer is reacted with water to form polyurethane foam. Carboxylic acid and/or other hydroxyl-containing compounds may be used in addition to or in place of water (Karol 1982a, Vinson and Mitchell 1972). This foam consists of crosslinked polyurethane chains with the crosslinking occurring through the formation of urea linkages accompanied by the generation of carbon dioxide gas (Vinson and Mitchell 1972, Billmeyer 1971).

Rather than complete the entire reaction at one time, the reaction sequence may be temporarily halted at the prepolymer formatin step with the final reaction of the prepolymer to form urethane foam being completed later. Many of the urethane grouts currently on the market consists only of the prepolymer; the polyurethane is generated from the prepolymer at the time of use.

In general, other materials may be added to the grout catalysts such as tertiary amines (triethylamine, triethanolamine, triethylenediamine) or tin salt to control the rate of gellation and foaming (Karol 1982a, Jiacai et al. 1982). Stabilizers and surfactants may be added to control the surface tension of the grout as well as the size of the bubbles (Karol 1982a, Jiacai et al. 1982). Since the prepolymer has a high viscosity, the grout may be diluted with a solvent such as acetone, xylene, ethyl acetate, or dichloromethane. Plasticizers such as dibutylphthalate may also serve as dilution agents (Jiacai et al. 1982).

---

*McCabe, K.W. Mobay Chemical Corporation, Pittsburgh, PA. Written communication with G. Hunt, JRB Associates, August 3, 1982.

Urethane Grout Properties--

Formulated urethane grouts range in viscosity from 20 to 200 cP (Karol 1982a, Sommerer and Kitchens 1980, Avanti International 1982). The type of isocyanate and hydroxylated compounds used in the grout are major determinants of viscosity (Tallard and Caron 1977a). The amount of diluent in the grout also affects viscosity. With no diluent, the viscosity may be several thousand cP; however, the viscosity is approximately 25 cP with 50 percent dilution (Jiacai et al. 1982).

The set time varies from several seconds to several minutes or hours (McCabe 1982, Avanti International 1982, Tallard and Caron 1977a). The set time can be controlled with acids, amines, alcohols, water, or polyol size. The set time can be shortened by increasing the water content, moving from a primary to a secondary or tertiary alcohol, or increasing the catalyst (amine) content (Vinson and Mitchell 1972, Tallard and Caron 1977a). It may also be lengthened by decreasing the size of the polyol or by adding an acid (Sommerer and Kitchens 1980, Vinson and Mitchell 1972).

If properly formulated, set urethane grouts resist most chemicals and other degradative processes. Set urethane grouts are reported to have good resistance to oxidation, shrinkage from drying, and biological agents. Some shrinkage of the grout may occur however, in response to water table fluctuations (Avanti International 1982, Billmeyer 1971).

The prepolymer used in urethane grouts is flammable. The prepolymer and its components have low toxicity with an LD_{50} of 5,000 mg/kg or more (Berry 1982, Avanti International 1982, Mobay Chemical Corporation 1982). Most of the grouting formulations contain some free toluene diisocyanate. Special handling and protective equipment are needed when working with the grout materials because they are eye, skin, and respiratory irritants (Berry 1982, Avanti International 1982).

Grout/Chemical Interactions--

Set polyurethane resins are reported to have good resistance to oxidation and solvents (Billmeyer 1971). If properly formulated, CR-250 (a polyurethane grout) resists most chemicals and solvents. Testing of this grout indicated that no visible changes occurred when it was subjected to dilute acetic acid, sulfuric acid, and hydrogen sulfide, as well as concentrated organic solvents (Avanti International 1982). Further testing of CR-250 indicated various amounts of shrinkage in response to hydrochloric acid, ethylene glycol, methyl ethyl ketone, ammonium and potassium sulfate, and sodium chloride. Swelling was noted in response to dilute hydroxides and isopropanol (Avanti International 1982).

Although the isocyanates in the grout react with water they can also react with carboxylic groups as well as hydrogen and nitrogen ion such as ammonia or ammonium hydroxide (Karol 1982a). The presence of these materials may interfere with proper reaction and setting of the grout. Preliminary results from a laboratory compatibility testing program undertaken by the U.S. Army Corps of Engineers Waterways Experiment Station has shown that the urethane grout tested would not set in the presence of low levels of any of the chemicals selected for their study.

Areas of Application--

Urethane grouts have been used in a number of waterproofing and soils applications. Some formulations have been used for consolidation grouting in coal mines and railroad tunnels (Mobay Chemical Corporation 1982). Other formulations are primarily used for sewer grouting and pipe sealing (Avanti International 1982). CR-250 has been used for potable water applications as well as soil sealing and waterproofing (Jacques 1981).

TACSS, a urethane grout produced in Japan, has been used for sealing voids in karst materials and for consolidating and waterproofing ground through which large volumes of water circulate (Tallard and Caron 1977a). Due to the high viscosity of this formulation (and by analogy, other urethane grouts), it cannot be used to treat fine grained soils (Karol 1982a).

Properties of Urea-Formaldehyde Grouts

Urea-formaldehyde resins are frequently referred to as aminoplasts. The idea for the use of these resins as grouts came from their use as glue. The oil industry the first to use these resins for grouting (Tallard and Caron 1977a). Although urea-formaldehyde grouts have been available since the 1960s, they have found limited usage (Karol 1982b, Sommerer and Kitchens 1980).

Chemical Composition and Reaction Theory--

Urea-formaldehyde resin grouts consist of urea, formaldehyde, a catalyst, and water. The urea-formaldehyde mixture may be in monomer or prepolymer form. The catalyst is an organic acid, inorganic acid, or acid salts. In Cyanaloc 62 (discontinued), the catalyst was sodium bisulfate (Karol 1982a, Kirk-Othmer 1979, Tallard and Caron 1977a, Chung 1973).

The urea-formaldehyde resin is formed in a two step reaction process. First, the urea and formaldehyde monomers react through methylolation or hydroxymethylation, to form low molecular weight polymers. This reaction may be either acid or base catalyzed (Kirk-Othmer 1978b). The second reaction involves further polymerization through condensation of the polymers with water being generated. This reaction will occur only with an acid catalyst (Kirk-Othmer 1978b, Billmeyer 1971). The resulting resin is a stable network of crosslinked urea-formaldehyde polymers (Tallard and Caron 1977a).

There are two mechanisms for achieving this reaction sequence. Where the grout mixture uses urea and formaldehyde monomers, the two reactions occur rapidly and the overall reaction is difficult to control (Karol 1982a). The second mechanism involves stopping the reaction sequence after methylolation. At this point, precondensates or prepolymers have formed which are soluble in water and are prevented from further reaction through the use of inhibitors or pH controls (Karol 1982a, Tallard and Caron 1977a). Commercially, the methylolation reaction is base catalyzed (Kirk-Othmer 1978b, Tallard and Caron 1977a). The second reaction, polymerization, may be caused later by lowering the pH of the prepolymer solution. By introducing an intermediate stage in the reaction, better gel time control is achieved and sudden setting of the grout can be avoided (Karol 1982a, Tallard and Caron 1977a).

In either case, an acid medium is required for final polymerization to occur. For this reason, urea-formaldehyde resins cannot be used in alkaline media. The acid catalyst will react with the media and be destroyed before it can react with the grout (Sommerer and Kitchens 1980, Tallard and Caron 1977a, Rensvold 1968). In addition to pH control, the urea-formaldehyde reaction is also controlled by the mole ratio of the reactants and dilution of the mixture (Kirk-Othmer 1978b, Tallard and Caron 1977a).

Urea-Formaldehyde Grout Properties--

Urea-formaldehyde grouts have a low viscosity. Urea solutions (unpolymerized) have viscosities similar to acrylamides and phenolics (Karol 1982a). Solutions of urea-formaldehyde prepolymers are more viscous, with typical formulations having a viscosity of 10 to 13 cP (Karol 1982a, Sommerer and Kitchens 1980).

The set time varies with the type of grout formulation and the type of catalyst. Monomer grouts have a very short set time because the reaction is abrupt. To achieve more control over the set time, prepolymer grouts are used. This however, increases the viscosity of the grout and makes it unsuitable for fine soils. Depending on the catalyst, the set time may vary from several minutes (hydrochloric acid) to almost an hour (sulfuric acid). The proportion of the catalyst and the dilution of the grout will also affect the set time (Tallard and Caron 1977a).

For urea-formaldehyde grouts there is both a gel time and a cure time. The gel time refers to the time to form a soft gel, similar to acrylamide. Following gellation, the grout cures to a stiffer consistency. This occurs over a few hours to as long as a day, with the rate dependent on the gel time (Karol 1982a).

Urea-formaldehyde grouts are considered permanent, with good stability (Karol 1982a). If the grout is properly formulated and a good polycondensation reaction is achieved, the resulting resin should be inert and insoluble to most solvents, although it will contain some free formaldehyde (Karol 1982a, Tallard and Caron 1977a). These grouts however, may quickly break down when subjected to cyclic wet/dry or freeze/thaw cycles (Karol 1982a). Fung (1980) reports that some urea-formaldehyde resins are biodegradable.

The grout solution is both toxic and corrosive because it contains formaldehyde and an acid catalyst. However, grout solutions using prepolymers have less free formaldehyde (Karol 1982a, Tallard and Caron 1977a). The cured resin has low toxicity. The resin is considered inert but it contains some unreacted formaldehyde (Kirk-Othmer 1978b, Tallard and Caron 1977a).

Grout/Chemical Interactions--

As mentioned above, if a good polymerization (condensation) reaction is achieved, the resulting resin is inert and insoluble in most solvents. In general, urea-formaldehyde grouts are compatible with acids, sulfates, and halides (Malone, Jones, and Larson 1980).

The setting of urea-formaldehyde grouts may be slowed by organic solvents and oils (Malone, Jones, and Larson 1980). Cement will prevent the setting of these grouts (Kirk-Othmer 1979). In general, alkaline materials will inhibit the polymerization reaction through destruction of the acid catalyst.

Upon setting, oxidizing agents such as chlorine or peroxides may cause the grout matrix to break down (Malone, Jones, and Larson 1980). Testing of Cyanaloc 62 (discontinued) determined that this urea-formaldehyde grout deteriorated and lost strength upon prolonged submergence in an acid solution (Chung 1973).

Finally, the acidity of the grout may affect surrounding materials. For example, the low pH of the grout can solubilize metal hydroxides (Malone, Jones, and Larson 1980). This can increase the mobility of these heavy metals.

Areas of Application--

Because of the acidity requirements, urea-formaldehyde grouts have undergone little development (Tallard and Caron 1977a). They have been used for ground stabilization and sealing coal mines but no long-term applications have been reported (Karol 1982a, Tallard, and Caron 1977a). These grouts can generally be used only in ground and groundwater with a pH less than 7. Their development is further limited due to their toxic constituents and the production of ammonia during condensation (Sommerer and Kitchens 1980).

Most of the descriptions of urea-formaldehyde grout applications come from Eastern Europe, the USSR, and Japan. Products containing prepolymers are used in Poland and Hungary. The USSR resolves the acid media problem through injection of an acid solution to destroy carbonates before injection of urea-formaldehyde. This technique, however, is not used outside of the USSR, is costly, and increases the size of soil voids. Further, soil instability may be created through destruction of soil components (Tallard and Caron 1977a).

Properties of Epoxy Grouts

Epoxy grouts, like other glue-like grouts, have been in use since around 1960. These grouts have had limited use in soil grouting primarily because of their high cost (Tallard and Caron 1977a).

Chemical Composition and Reaction Theory--

Epoxy grouts are resins that consist of an epoxide, a hydroxy compound, and a hardener. The epoxide is typically epichlorohydrin, while the hydroxy compound is typically bis-phenol A (2,2-bis(4-hydroxyphenol) propane) (Modern Plastics Encyclopedia 1981, Tallard and Caron 1977a, Billmeyer 1971).

Epoxies are generally cured through the addition of a hardener (Tallard and Caron 1977a). These hardeners are crosslinking agents which react with epoxy and hydroxyl groups (Modern Plastics Encyclopedia 1981). The resulting epoxy resins are polyethers (Billmeyer 1971).

A number of hardeners may be used. Typically, amines, polycarboxylic anhydrides, or monocarboxylic acids are used. Each hardener reacts differently, and imparts different properties to the resin. Different proportions between the resin and the hardener will also provide different types of resins. The resin-hardener ratio, however, cannot be varied greatly (Tallard and Caron 1977a).

As a result of the amine hardening process, amine-terminated polyamide resins are generated. These resins replace water on wet surfaces creating a water-free interface between the resin and the material covered (Engineering News-Record 1965). For this reason, epoxy resins are useful in applications in wet areas or under water.

Epoxy Grout Properties--

The viscosity of epoxy grouts varies with the molecular weight (Billmeyer 1971). The most fluid of these resins has a viscosity of at least 400 cP. This viscosity may be lowered to 100 cP through the addition of a fluid hardener (Tallard and Caron 1977a). Organic solvents and reactive dilution substances may also be used to alter the viscosity (Sommerer and Kitchens 1980, Tallard and Caron 1977a). Ethers such as butyl glycidyl ether can further decrease the viscosity of epoxy grouts to 20 cP (Tallard and Caron 1977a).

The set time of epoxy grouts varies depending on the choice of hardener. In general, the set time is difficult to regulate (Tallard and Caron 1977a).

Epoxy grouts have good durability. In the ground, their properties are similar to those of the polyesters which may be subject to hydrolysis (Tallard and Caron 1977a). Epoxy mortars tend to have little shrinkage and limited water absorption (U.S. Grout Corporation 1981, Boova 1977).

Epoxy grouts consist of substances requiring special handling precautions. If the grouts are properly formulated, resin formation should incorporate all of the materials and the toxicity of the gel or its components will be minimized (Tallard and Caron 1977a).

Grout/Chemical Interactions--

Chemical resistance and incompatibility data were available primarily for epoxy resin mortars rather than grouts. These mortars are similar to the grouts, although they often contain fillers which may alter the resistance of the epoxy resin. The reported resistances are generally for immersion of the resin in the media in question.

In general, epoxy grouts are resistant to acids, alkalis, and organic chemicals (Office of the Chief of Engineers 1973). Epoxy resin mortars are recommended for nonoxidizing mineral acids (except sulfuric acid and hydrofluoric acid), inorganic alkalis, wet gases (reducing), and nonoxidizing and nonreducing gases (except ammonia) (ASTM 1982). These mortars are also recommended for ethyl alcohol, gasoline, hydrochloric acid, sodium chloride, and sodium hydroxide (25%) (Boova 1977).

Epoxy resin mortars are not recommended for use with ammonia, wet gases (oxidizing), glacial acetic acid, benzene, chromic acid (20%), hydrofluoric acid, dichloroacetic acid (10%), sodium hypochlorite (10%) trichloroethylene, and xylene (Boova 1977, ASTM 1982). ASTM (1982) reports limited application of resin mortars in presence of oxidizing mineral acids, organic acids, bleaches, and organic solvents.

Areas of Application--

Epoxy resins are infrequently used for soil grouting because of their high cost (Tallard and Caron 1977a). Most of the applications reported in the literature have addressed the use of epoxy resins in mortars used for sealing cracks. Epoxy resins can adhere to and seal submerged concrete, steel, or wood surfaces and are useful in waterproofing applications (Engineering News-Record 1965). They have been used for grouting of cracked concrete for structural repairs, and grouting fractured rock to improve its strength (Office of the Chief of Engineers 1973).

Properties of Polyester Grouts

Polyester grouts have been in use since the 1960s, and have been used in a variety of construction applications. These grouts, however, are generally suitable only for very specific applications (Tallard and Caron 1977a).

Chemical Components and Reaction Theory--

Polyester grouts consist of a resin base and a catalyst (Office of the Chief of Engineers 1973). The resin is unsaturated and consists of a polyester produced from the reaction of a polyacid and polyalcohol. Typically, this reaction involves the condensation of an unsaturated diacid (maleic acid or fumaric acid) with a dialcohol. In commercial products, a reticulant is included with the polyester resin. These products may contain 30 to 40 percent reticulant, typically styrene (Tallard and Caron 1977a, Billmeyer 1971).

Polymerization is achieved through addition of the catalyst, which is generally a peroxide. The catalyst causes the polyester resin to polymerize as well as copolymerize with the reticulant. A gel forms which eventually hardens to a solid material (Tallard and Caron 1977a, Office of the Chief of Engineers 1973). The hardening process is accompanied by shrinkage of the resin by as much as 10 percent (Office of the Chief of Engineers 1973).

Accelerators may be added to speed up the setting by facilitating the decomposition of the catalyst into free radicals (Tallard and Caron 1977a, Office of the Chief of Engineers 1973). Accelerators include cobalt, manganese, or vanadium salts; mercaptans; tertiary amines; and quaternary ammonium salts (Tallard and Caron 1977a).

The quantity and type of polyester, reticulant, and catalyst may each be varied and each variation will produce different resins with different characteristics (Tallard and Caron 1977a).

Polyester Grout Properties--

Commercial polyesters vary in viscosity from several hundred to several thousand cP. The minimum viscosity is between 200 to 250 cP. This, however, is too high to grout even coarser earth materials such as sand. The viscosity, though, can be reduced to 10 to 50 cP by adding a reactive diluent (Tallard and Caron 1977a).

The set time of polyester grouts varies from a few minutes to several days and the resins may contain volatile compounds that make long set times uncertain (Tallard and Caron 1977a). The set time can be controlled through resin volume, ambient temperature, catalyst selection, and heat dissipation (polymerization is exothermic). In addition, excessive moisture may inhibit the setting of polyester grouts (Office of the Chief of Engineers 1973).

The long-term behavior of polyester grouts is reported to be good, however, there is a long-term risk of hydrolysis particularly in alkaline media (Tallard and Caron 1977a). Further, these gels shrink during curing and this shrinkage may be as high as 10 percent (Office of the Chief of Engineers 1973).

The components of the polyester grouts are toxic and require special handling during grout preparation. After polymerization, the risks are less (Tallard and Caron 1977a). Unreacted constituents in the polymerized grout, however, may be leached out.

Grout/Chemical Interactions--

Available information addressed the chemical resistance of polyester resin mortars which are similar to polyester grout except that they contain fillers (Boova 1977). These materials were rated based on immersion in the chemicals.

Polyester resin mortars are recommended for chlorine dioxide, gasoline, hydrochloric acid, nitric acid, sulfuric acid (50 percent), sodium chloride, ethyl alcohol, lactic acid, phosphoric acid, sodium hydroxide (25 percent), and sodium hypochlorite (10 percent) (Boova 1977). In general, these mortars are resistant to nonoxidizing mineral acids (except for sulfuric acid [$\geq$ 85 percent] and hydrofluoric acid), bleaches, wet gases (oxidizing and reducing), and nonoxidizing and nonreducing gases (ASTM 1982). They have limited use for organic acids, oxidizing mineral acids, xylene, and trichloroethylene (ASTM 1982, Boova 1977).

Polyester resin mortars are not recommended for use with glacial acetic acid or benzene (Boova 1977). In general, these mortars are not recommended for inorganic alkali or organic solvents (ASTM 1982).

Areas of Application--

Polyester grouts have been used in a variety of construction applications, but are principally used to treat cracks in buildings and structures (Tallard and Caron 1977a). These grouts have also been used in mines to stabilize and strengthen porous and fissured rock (Tallard and Caron 1977a, Office of the Chief of Engineers 1973). Polyester grouts have been used infrequently to consolidate sand (Tallard and Caron 1977a).

In general, polyester grouts have limited suitability. They can be used for injection, although they are not recommended for materials with large voids due to shrinkage during curing (Tallard and Caron 1977a).

PROPERTIES OF OTHER GROUTS

There are a number of other grout types available that have either limited or questionable use in soils, or are no longer used. These grouts and their properties are briefly summarized.

Properties of Lignochrome Grouts

Lignochrome grouts are also referred to as lignosulfonate or chrome-lignin grouts. This type of grout consists of a lignin-containing material and a hexavalent chromium salt (Kirk-Othmer 1979, Ingles and Metcalf 1973). Calcium lignosulfates provide better waterproofing and stability than sodium lignosulfates (Rogoshewski et al. 1980). Ammonium lignosulfonate may also be used (Sommerer and Kitchen 1980). Potassium dichromate may be used as the hexavalent chromium salt (Ingles and Metcalf 1973).

In the presence of an acid, the lignosulfate is oxidized by the hexavalent chrome to form a gel (Sommerer and Kitchens 1980, Bowen 1981, Ingles and Metcalf 1973). During this reaction, hexavalent chromium is reduced to the trivalent form (Rogoshewski et al. 1980). The set time is controlled by the concentration of hexavalent chromium, acid, water, and the catalyst (typically another metal salt) (Rogoshewski et al. 1980, Sommerer and Kitchens 1980). During injection, the grout may be diluted by groundwater and this can increase the set time (Office of the Chief of Engineers 1973).

Lignochrome grouts typically have low viscosities (2-15 cP) and moderately short setting times (3-300 minutes). The durability of these grouts is questionable, as their strength decreases over time in water-saturated environments (Kirk-Othmer 1979). Also, chromium can be leached from the set grout (Sommerer and Kitchens 1980). This process depends on the age of the grout, the chrome-lignin ratio, the acidity (pH), and curing time (Sommerer and Kitchens 1980, Office of the Chief of Engineers 1973).

The chromium salts used in lignochrome grouts are highly toxic. In addition, the lignin materials can cause skin irritation (Kirk-Othmer 1979).

Little information was available regarding the compatibility of these grouts with chemicals. Lignochrome grouts should not, however, be used with

Portland cement because the pH of the materials conflict (Kirk-Othmer 1979). Further, lignochrome grouts are not compatible with fly ash because its alkalinity can cause trivalent chromium to precipitate from the dichromate catalyst (Chung 1973).

Lignochrome grouts have primarily been used for water cut-off and consolidation of fine, granular soil (Office of the Chief of Engineers 1973). They can be used in sands with a permeability between 10^{-1} and 10^{-3} cm/sec (Sommerer and Kitchens 1980). Lignochrome grouts have been used in water cut-off applications for dams (Engineering News-Record 1953). These grouts appear to have little use at this time, and are currently not manufactured in the United States.

Properties of Furan Grouts

Furan grouts consist of low polymers of furfuryl alcohol dissolved in excess furfuryl alcohol. For furan mortar grouts, the liquid resin is mixed with an inert powder filler (usually carbon) containing an acid catalyst. This catalyst promotes further polymerization to form a crosslinked, infusible material (Boova 1977).

Furan grouts have been referenced in the literature largely with respect to their use as mortars. They provide a broad range of chemical resistance to organic and inorganic acids, alkali, salts, greases, and solvents (Boova 1977). These grouts have excellent resistance to acids and almost all alkali (Boova 1977). They are not recommended, however, for oxidizing acids in general, as well as chromic acid (20%), nitric acid, sodium hypochlorite (10%), or concentrated sulfuric acid (Boova 1977, ASTM 1982).

These resin grouts are used in applications where resistance to corrosive media is important. They are also used for polymer concrete. This concrete consists of alkali-free aggregate (silica or quartz) that is bonded with furan resins and cured with an acidic catalyst. This concrete is resistant to acids, salts, solvents, and bases (Modern Plastics Encyclopedia 1981).

Miscellaneous Grouts

Several other types of grouts have been referenced with regard to soil applications. The majority of these materials are polymers. One such grout, Polythixon FRD, is an oil-based unsaturated fatty acid polymer. It has low viscosity (10-80 cP) and a gel time of 25 to 360 minutes. This grout is recommended for high strength consolidation rather than waterproofing applications (Neelands and James 1963).

Another polymer grout is PWG sealant, a polymerized crosslinked gel (unspecified polymer). This grout has very low viscosity (1.5 cP) and a very short set time (several seconds to more than a minute). The set gel is insoluble in water, kerosene, and oil, and is impermeable to water, oil, and gases. If the gel dehydrates, it can rehydrate in the presence of water to regain its original size. In addition, this gel may undergo "wicking," i.e., if one "face" of the gel dehydrates, moisture can move from the hydrated "face" to the dehydrated "face" (Lenahan 1973).

Aniline-furfural resins may be used for the stabilization of cohesionless sand. These resins are catalyzed by pentachlorophenol or ferric chloride (Bowen 1981). Also, emulsions such as latex and salt water, styrene butadiene latex, and pitch polyurethane mixtures may be used a grouts (Bowen 1981).

Base-cured materials have been investigated for use as grouts. These materials do not, however, have low viscosity or other characteristics that lend them to injection at pressures that will not disturb the formation (Rensvold 1968).

SECTION 6

COMPATIBILITY OF GROUTS WITH HAZARDOUS WASTES

Through a detailed evaluation of available information on the effects of chemicals on grout performance, a series of matrices were developed that summarize and define the compatibilities of grouts with various chemical groups. This information was gathered through contacts with representatives from universities, industries, trade associations, and government agencies along with a detailed review of the published literature. The literature sources, listed in the bibliography, contained not only grouting related publications but also references on waste fixation/solidification, cement chemistry, landfill/lagoon linear performance, slurry wall construction, and polymer chemistry as well as performance specifications for cement, coatings, and tile grouts.

From the information obtained, three matrices were developed which summarize and define the compatibilities of grouts with various chemical groups. These matrices provide a step-wise analysis of the data, moving from general to specific information that has been found. It must be noted, though, that most of the information detailed the effects of pure chemicals or did not specify a concentration. Thus, this data can be assumed to be related to the effects of undiluted chemicals. While leachates generally contain low levels of compounds, there can be instances where grouts will come into contact with high concentrations of chemicals, such as organic solvent lenses within the groundwater system.

The following subsections present the matrices along with a discussion of matrix development, data sources, and limitations.

KNOWN COMPATIBILITY OF GROUTS WITH CLASSES OF CHEMICALS

The structure of the matrices is as follows: the types of grouts, on the horizontal axis, are correlated with the chemical groups on the vertical axis. These two parameters are linked by codes that represent the type of compatibility/incompatibility of the chemicals and grouts. An overview of each of the grout types and chemical groups utilized in these matrices along with the compatibility index is contained in the following discussions.

Grout Classes

Based on the results of our information search, six categories of grouts that potentially could be used for construction at hazardous waste sites were selected for inclusion in our study. These categories are:

- Bitumen
- Portland Cement
    - Type I
    - Type II and V
- Clay (Bentonite)
- Clay-Cement
- Silicates
- Organic Polymers
    - Acrylamide
    - Phenolic
    - Urethane
    - Urea-formaldehyde
    - Epoxy
    - Polyester.

A detailed discussion of the chemical characteristics, reaction theory, physical/chemical properties, and areas of application of each of these grouts can be found in Section 3.

Chemical Groups

In order to reduce the complexity of the matrix, the chemical universe was divided into 16 basic groups as follows:

- Alcohols and Glycols
- Aldehydes and Ketones
- Aliphatic and Aromatic Hydrocarbons
- Amines and Amides
- Chlorinated Hydrocarbons
- Ether and Epoxides
- Heterocyclics
- Nitriles
- Organic Acids and Acid Chlorides
- Organo-metallics

- Phenols
- Organic Esters
- Heavy Metal Salts and Complexes
- Inorganic Acids
- Inorganic Bases
- Inorganic Salts.

The choice of the 16 basic groups was not meant to be all inclusive, but rather, a representative choice of the types of compounds found in landfills. The organic categories were chosen by functional group or structural characteristic; the inorganics are essentially divided into the classical acid/base/salt categories. The functional grouping for the organics is useful because, although their physical properties and solubilities may differ, the interaction of a particular functional group with other groups remains the same. For example, all amines may not be soluble in water, but they all can be halogenated. In addition, one chemical may fit in more than one category if it has more than one functional group. For example, p-aminobenzoic acid is both an amine and an organic acid. The amine and acid moieties will chemically act independently of one another although the reactivity may be modified to some extent by the presence of the new group.

The following subsections outline the chemical structure and properties that separate the different groups of chemicals. Examples of compounds contained in each of the chemical groups are given in Table 7.

Alcohols and Glycols--

Alcohols and glycols both contain hydroxyl (-OH) groups and are grouped together because of that common functionality. Alcohols are aliphatic or aromatic compounds that contain a single hydroxyl (-OH) group. This group excludes compounds where the hydroxyl group is attached directly to an aromatic ring, because these compounds are phenols and have very different properties and reactions than alcohols. The lower alcohols (containing small aliphatic groups) are miscible with water and are capable of hydrogen bonding. Higher alcohols (containing aromatic or large aliphatic groups) have a much larger organic component and are much less miscible in water and less able to form hydrogen bonds.

Glycols are dihydroxy alcohols. These substances are aliphatic or aromatic compounds that contain two hydroxyl groups. As with alcohols, lower glycols have a greater miscibility in water. Glycols containing as many as 7 carbon atoms are soluble in water.

Aldephydes and Ketones--

Aldehydes and ketones both contain a carbonyl group (C=O). In aldehydes, the carbonyl group is attached to one organic group (aliphatic or aromatic), thus, the carbonyl group appears at one "end" of the compound. Ketones, however have two organic groups (aliphatic or aromatic) attached to

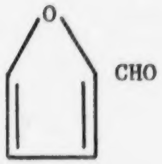
TABLE 7. EXAMPLES OF CHEMICALS WITHIN EACH OF THE CHEMICAL GROUPS

ALDEHYDES AND KETONES

Examples of Aldehydes

$CH_2 = CH\ CHO$

Acrolein



Furfural

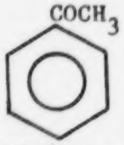
Examples of Ketones

$CH_3\ COCH_2\ CH_3$

Methyl Ethyl Ketone

$CH_3\ COCH_3$

Acetone



Acetophenone

TABLE 7. (Continued)

ALCOHOLS AND GLYCOLS

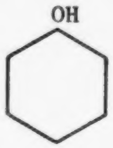
Examples of Alcohols

$CH_3\ CH_2\ OH$

Ethanol

$CH_3\ OH$

Methanol



Cyclohexanol

Examples of Glycols

$CH_2\ OHCHOHCH_3$

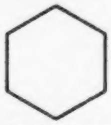
1,2-Propanediol

$CH_2\ OHCH_2\ OH$

Ethylene Glycol

ALIPHATIC/AROMATIC HYDROCARBONS

Examples of Aliphatic Hydrocarbons



Cyclohexane

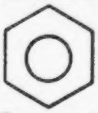
$CH_3 - CH_2 - CH_2 - CH_2 - CH_2 - CH_3$

n-Hexane

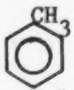
$CH_2 = CH - CH = CH - CH_3$

1,3-Pentadiene

Examples of Aromatic Hydrocarbons



Benzene

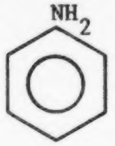


Toluene

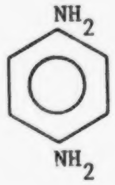
TABLE 7. (Continued)

AMINES AND AMIDES

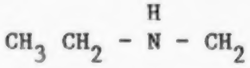
Examples of Amines



Aniline

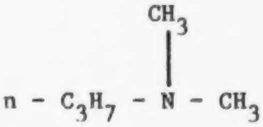


p-Phenylenediamine



$$CH_3\ CH_2 - \overset{H}{N} - CH_2$$

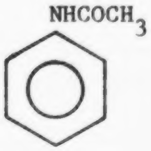
Methylethyl amine



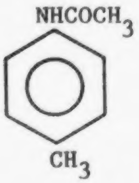
$$n - C_3H_7 - \overset{CH_3}{\overset{|}{N}} - CH_3$$

n - propyldimethylamine

Examples of Amides



Acetanilide



Aceto-p-toluidide

TABLE 7. (Continued)

ETHERS AND EPOXIDES

Examples of Ethers

$CH_2\ Cl - O - CH_2 - Cl_2$

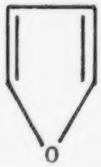
Bis (Chloromethyl Ether)

$CH_3\ CH_2 - O - CH_2\ CH_3$

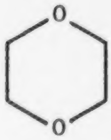
Diethyl Ether

$Cl\ CH_2\ CH_2 - O - CH = CH_2$

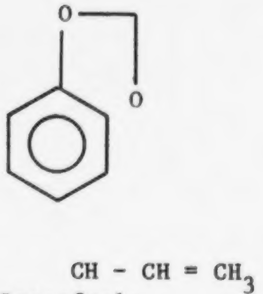
2-Chloroethyl Vinyl Ether



Furan

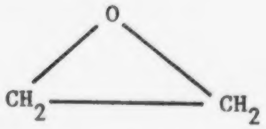


1,4-Dioxane



Isosafrole

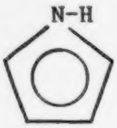
Examples of Epoxides



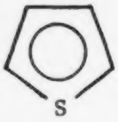
Ethylene Oxides

TABLE 7. (Continued)

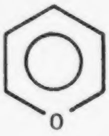
HETERCYCLICS



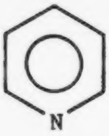
Pyrrole



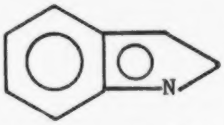
Thiophene



Tetrahydrofuran

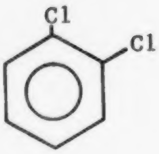


Pyridine

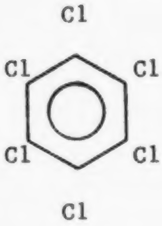


Indole

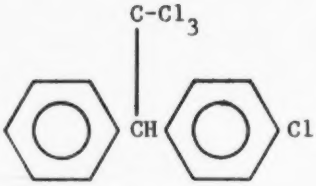
CHLORINATED HYDROCARBONS



1,2-dichlorobenzene


Cl
Cl
Cl
Cl
Cl
Cl

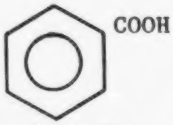
Hexachlorobenzene



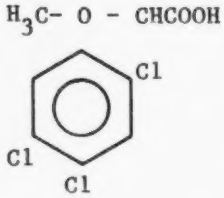
DDT

ORGANIC ACIDS

Organic Acids - carboxylic



Benzoic Acid


H3C- O - CHCOOH
Cl
Cl
Cl

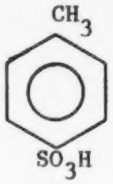
Silvex
2 (2,4,5-Trichlorophenoxy)propionic Acid

H_2COOH

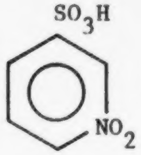
Formic Acid

TABLE 7. (Continued)

Organic Acids - sulfonic



p-Toluenesulfonic Acid



m-Nitrobenzenesulfonic Acid

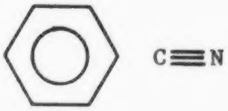
NITRILES

$CH_3 \quad N$

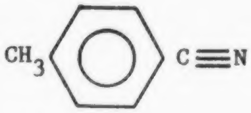
Acetonitrile

$CH_3\ (CH_2)_3C \quad N$

n-Valeronitrile

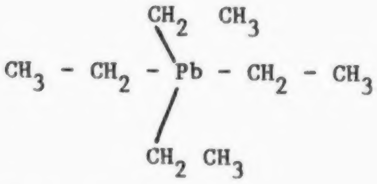


Benzonitrile

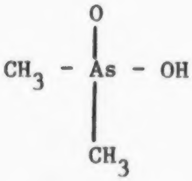


p-Tolunitrile

ORGANOMETALLIC COMPOUNDS



Tetraethyl Lead

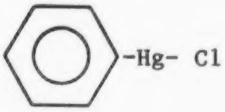


$$CH_3 - \overset{\overset{\displaystyle O}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{As}} - OH$$

Cacodylic Acid

$CH_3\text{-}Hg\text{-}Cl$

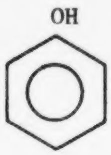
Methylmercuric Chloride



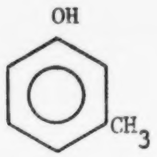
Phenyl Mercuric Chloride

TABLE 7. (Continued)

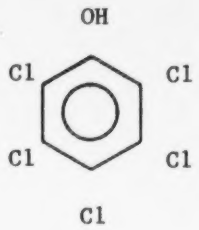
PHENOLS



Phenol



m-Cresol



Pentachlorophenol

INORGANIC ACIDS	
Sulfuric Acid	H_2SO_4
Nitric Acid	HNO_3
Hydrochloric Acid	HCl
Phosphoric Acid	H_3PO_4
HEAVY METAL SALTS AND COMPLEXES	
Chromium Hydroxide	$Cr(OH)_2$
Zinc Cyanide	$Zn(CN)_2$
Cadmium Chloride	$Cd\ Cl_2$
Nickel Cyanide	$Ni(CN)_2$
INORGANIC BASES	
Sodium Hydroxide	$NaOH$
Potassium Hydroxide	KOH
Calcium Hydroxide	$Ca(OH)_2$

TABLE 7. (Continued)

INORGANIC SALTS	
Sodium Chloride	$NaCl$
Magnesium Sulfate	$MgSO_4$
Calcium Bisulfite	$Ca(HSO_3)_2$
Potassium Nitrate	KNO_3

the carbonyl group, thus, the carbonyl groups appear in the "middle" of the compound.

Aldehydes and ketones are polar compounds. The lower ones are soluble in water and in organic solvents such as ethanol and ether. Aldehydes and ketones containing more than 5 carbon atoms are not soluble in water. In general, aldehydes are more reactive with bases and more readily oxidized than ketones.

Aliphatic/Aromatic Hydrocarbons--

Hydrocarbons are compounds that contain carbon and hydrogen as the basic structural part of the molecule. Examples of hydrocarbons are methane, ethane, acetylene, benzene, n-hexane, and toluene. Many hydrocarbons are used as organic solvents, and have been found in leachate from landfills (Shuckrow et al, 1980). In general, they can be volatile, especially the lower molecular weight compounds, and have been low water solubilities. In general, the liquid hydrocarbons are lighter than water and will form a layer on the surface of water. This is especially true of the more prevalent solvents. Hydrocarbons are not expected to be particularly reactive under conditions in landfills, although hydrocarbons containing a carbon-carbon double bond may be subject to addition at that bond under certain conditions. For example, the double bond may hydrate under acidic conditions to form an alcohol.

Amines and Amides--

Amines and amides are nitrogen-containing organic compounds. Amines contain nitrogen that is attached to one, two, or three aliphatic and aromatic groups, thus, they have the general formula RNH_2, R_2NH, and R_3N, where R represents an aliphatic or aromatic group. Examples of amines are aniline, p-phenylene- diamine, and benzidine. Amines are polar compounds, can form hydrogen bonds with water, and are basic. Higher molecular weight amines (greater than six carbon atoms) are not soluble in water, but the lower molecular weight compounds are soluble at least to some extent. Amines are soluble in less polar solvents such as ether, alcohol, and benzene.

Amides contain nitrogen that is attached to a carbonyl group (C=O). They have the general formula of $R\text{-}CONH_2$, R-CONH-R, and $R\text{-}CON\text{-}R_2$, where R may be an aliphatic or aromatic group. Amides, like amines, are polar compounds and are capable of strong hydrogen bonding. Amides containing up to five or six carbon atoms are soluble in water. Higher molecular weight amides are generally not water soluble.

Ethers and Epoxides--

Ethers consist of two compounds (aromatic or aliphatic) that are attached by an oxygen atom; thus, ethers have the general structure R-O-R, where R is either an aromatic or aliphatic group. Ethers are somewhat soluble in water (comparable to the solubility of alcohols) and are comparatively unreactive compounds. Ethers are stable toward bases, oxidizing agents, and reducing agents.

Epoxides contain a three-member ring consisting of two carbon atoms and one oxygen atom. They are grouped with ethers because they have the R-O-R linkage, but their ring structure makes them highly reactive, particularly to acids and bases.

Heterocyclics--

Heterocyclic compounds are single or multi-ring compounds with the ring(s) containing more than one kind of atom. In addition to carbon, heterocyclic rings often contain sulfur, nitrogen, or oxygen. These rings can either be aliphatic or aromatic. Five-membered aromatic heterocyclics are fairly reactive. Of the six-membered rings, pyridine is the most common; pyridine is a weak base.

Halogenated Hydrocarbons--

Halogenated hydrocarbons are aliphatic or aromatic compounds that also contain halogens, such as chloride or bromide. In general, the more halogen atoms present, the less water soluble the compound is. These compounds, as a class, are unable to form hydrogen bonds and are stable.

Organic Acids and Acid Chlorides--

The two major classes of organic acids are carboxylic and sulfonic acids. Carboxylic acids contain a carboxyl group (COOH) attached to an organic group (aliphatic or aromatic). The lower carboxylic acids are soluble in water; the higher acids (containing 5 or more carbon atoms) are insoluble. Carboxylic acids are soluble in less polar solvents such as ether, alcohol, and benzene. These acids can form hydrogen bonds. Carboxylic acids containing more than eight carbon atoms are solids. Sulfonic acids contain sulfur and are more acidic than carboxylic acids. The sulfur is bonded directly to a carbon atom, and the general formula is $R-SO_3H$. As a class, these compounds are more soluble in water than any other organic compounds, but are insoluble in organic solvents such as diethyl ether, benzene, and carbon disulfide. The SO_3H group is often used to make otherwise insoluble compounds soluble, especially in the dye industry. Both types of acids form salts with cations.

Acid chlorides are functional derivatives of carboxylic acids; the hydroxyl group (-OH) of the carboxylic acid has been replaced by chloride (-Cl). An example is acetyl chloride, CH_3COCl. Acid chlorides may contain an aliphatic or aromatic group. Acid chlorides are polar compounds and are soluble in organic solvents. Only the simpler acid chlorides are soluble in water.

Nitriles--

Nitriles are organic compounds that contain a cyanide group (C N). Upon hydrolysis, nitriles form acids. Acetonitrile, a simple nitrile, is a widely used non-aqueous solvent.

Organometallic Compounds--

Organometallic compounds consist of organic compounds (aliphatic or aromatic) and a metal such as chromium, cadmium, lithium, iron, cobalt, nickel, or copper. These compounds play an important role as catalysts in many chemical reactions. Some of the complex organometallic substances such as hemoglobin or chlorophyll are important biological materials. Organometallics containing arsenic and cadmium are used as pesticides. Tetraethyl lead is used as an antiknock agent in gasoline. In general, organometallics are resistant to degradation under ambient conditions, although arsenicals are degraded rather quickly to arsine by biological action. Organometallics such as tetraethyl lead are insoluble in water, but soluble in non-polar organic solvents.

Phenols--

Phenols are aromatic compounds that have a hydroxyl (-OH) group attached directly to the aromatic ring. The ring may have other groups attached; cresols, for example, have an -OH and a $-CH_3$ group attached to the ring. Most of the phenols are insoluble in water although phenol itself is somewhat soluble. These compounds are capable of hydrogen bonding, easily oxidized, and fairly acidic. The lower molecular weight phenols are liquids or low melting solids. Boiling points tend to be high because of hydrogen bonding.

Organic Esters--

Esters are the products of the reaction of acids with alcohols or phenols. This reaction may be seen as comparable to the reaction of an inorganic acid and inorganic base to form a salt. Low molecular weight esters generally have a pleasant odor and are relatively unreactive. They are not particularly soluble in water, but some, such as ethyl acetate are good solvents. Esters occur naturally in animal and vegetable fats and ordinary soap is made from fatty acid esters and sodium hydroxide.

Inorganic Acids--

Inorganic acids are compounds which produce H^+ groups when they dissociate. These compounds are readily soluble in water and will react with bases to form salts.

Heavy Metal Salts and Complexes--

Heavy metals encompass a wide range of elements, with the environmentally important ones being cadmium, chromium, copper, lead, mercury, nickel, silver, and zinc. Under the conditions normally found in groundwater systems, these metals can form complexes with a number of inorganic and organic compounds including SO_4^{-2} CN^-, OH^-, and EDTA. The pH of the system will control the solubility and the chemical form of the complexes.

Inorganic Bases--

Inorganic bases are compounds which produce an OH^- group when they dissociate. These compounds are soluble in water and will react with inorganic acids to form salts.

Inorganic Salts--

Salts are compounds consisting of metals (such as sodium, calcium, and potassium) combined with various non-metals (such as chloride, sulfate, and nitrate). The solubility of these compounds will vary with the constituent compounds. For example, most salts of Group I elements (lithium, sodium, potassium, rubidium, and cesium) are quite soluble in water.

Compatibility Index

From the literature and our analysis, there are two general aspects of grouts that may be affected by chemicals: set time of the grout and its durability once it is set. The numerical codes developed for the chemical compatibility matrices define the effect of the chemical classes on grout set time:

1. No significant effect
2. Increase set time (lengthen or prevent from setting)
3. Decrease set time.

The alphabetic codes relate to the durability of the grout (after setting) in the presence of chemicals:

a. No significant effect

b. Increase durability

c. Decrease durability (destructive action begins within a short time period)

d. Decrease durability (destructive action occurs over a long time period).

A question mark on the matrices indicates where information is not available for one or the other of the codes, or both.

It should be noted that the matrix codes only address changes in set time or durability as a result of exposure to chemicals. The codes do not address the specific mechanisms that lead to changes in set time or durability nor do they address mechanisms other than chemical action. For example, bacterial action can destroy some grouts, thus, the bacteria affect the durability of these grouts; this form of grout destruction is not included in the matrix.

Compatibility Matrices

Figure 5 presents a matrix defining the interactions between grouts and six general chemical classes: acids, bases, polar solvents, nonpolar solvents, heavy metals, and salts. The chemical groups that are included under each of these general classes are shown in Table 8. The data contained in this matrix were derived from both specific chemical information and general information regarding classes of chemicals. Much of the available data refer to the effect of general classes, such as salts or solvents, and not specific chemicals. These data were derived from available literature and conversations with industry and persons knowledgeable about grouts. Predictions or estimations of grout/chemical interactions are not included in this matrix.

Figure 5. Interactions Between Grouts and Generic Chemical Classes

Grout Type / Chemical Group	Bitumen	Portland Cement		Clay (Bentonite)	Clay-Cement	Silicate	Polymers					
		Type I	Type II and V				Acrylamide	Phenolic	Urethane	Urea-formaldehyde	Epoxy	Polyester
Acid	?a[§]	1d	1a	?c►	?c	3a	2c	?a[§]	2c	1d	?a[§]	?a[§]
Base	?a	1a	1a[†]	?c►	?d	2c	3d	?d	?d	2c	?a	?d
Heavy Metals	?d	2c	2a	?d	2c	3?	2?	?	?	?a	?	?
Non-Polar Solvent	?d	2d	2d	?d	?	?	?a	?d	?a	2a	?d	?d
Polar Solvent	?d	2c	2?	?d	?	?	?a	3a	3a	2?	?d	?d
Inorganic Salts	?d	2c	2a	2d	?d[*]	3?	3d[☆]	3a	?d	?a	?a	?a

KEY: Compatibility Index

Effect on Set Time

1 No significant effect
2 Increase in set time (lengthen or prevent from setting)
3 Decrease in set time

Effect on Durability

a No significant effect
b Increase durability
c Decrease durability (destructive action begins within a short time period)
d Decrease durability (destructive action occurs over a long time period)

* Except sulfates, which are ?c
† Except KOH and NaOH, which are 1d
☆ Except heavy metal salts which are 2
§ Non-oxidizing
► Modified bentonite is d
? Data Unavailable

Table 8. Constituents of the General Chemical Classes

- Acids
  - Inorganic Acids
  - Organic Acids and Acid Chlorides

- Bases
  - Inorganic Bases
  - Amides and Amines

- Heavy Metals
  - Organometallics
  - Heavy Metal Salts and Complexes

- Polar Solvents
  - Alcohols and Glycols
  - Aldehydes and Ketones
  - Ethers and Epoxides
  - Nitriles
  - Hetrocyclics

- Non-Polar Solvents
  - Aliphatic and Aromatic Hydrocarbons
  - Chlorinated Hydrocarbons

- Inorganic Salts

Figure 6 presents a more detailed matrix, where the chemical groups are more specific. Sixteen chemical classes are represented and have been divided into two categories: organic and inorganic. This matrix provides a more detailed understanding of the types of chemicals that may have a detrimental effect on grouts. The chemical classes presented in this matrix were defined in the previous section on chemical groups. Like the general matrix, Figure 6 does not contain any predictions or estimations of chemical/grout interactions. Only direct compatibility data are presented.

PREDICTED COMPATIBILITY OF GROUT WITH CLASSES OF CHEMICALS

In order to fill the information gaps, a matrix was developed that contains predictions or estimates of grout/chemical interactions. These predictions are based on the chemical structure, reaction theory, and estimated behavior of grouts in the presence of the various chemical groups. In order to make these estimations, a number of assumptions were made; these assumptions are described in detail below.

For the purposes of this report, typical landfill leachate is defined as having the following properties:

- High salt content
- Organic compounds will be approximately 1% in the leachate, although some may be in the ppm range
- Metal ions individually will not exceed 1%
- The pH will range from moderately acidic (pH 3) to moderately basic (pH 11).

The groundwater may be considered a multicomponent dilute solution. It will be further assumed that interactions between the components do not occur, but that interactions between the grout and each of the separate components may occur. These reactions will be considered to be free of interference from the other components. Because groundwater has no turbulence and is slow moving, the groundwater can be thought of as essentially static in nature. In such cases, it is possible that chemicals which are insoluble in water may form a layer either on top or on the bottom of the groundwater depending on their densities. Although these layers would be expected to be thin due to the low concentration of contaminants, the point of contact with the grout would be would be essentially "pure" contaminant, rather than a very dilute solution. This point of contact may then represent a special case and be a point at which an incompatibility may result in a critical weakening of the grouted structure. For example, if a thin layer of organic solvents formed on top of the groundwater and the grout was either solubilized or reacted with these solvents, the structure would be breached at that point. Once breached, the solvents could then penetrate more deeply resulting in a general weakening or alteration of the grout matrix.

Figure 6. Interactions Between Grouts and Specific Chemical Groups

Grout Type / Chemical Group		Portland Cement					Polymers					
	Bitumen	Type I	Type II and V	Clay (Bentonite)	Clay-Cement	Silicate	Acrylamide	Phenolic	Urethane	Urea-formaldehyde	Epoxy	Polyester
Organic Compounds												
Alcohols and Glycols	?a	?d	?d	?d	?d	?	?d	?	3a	?	?a	?a
Aldehydes and Ketones	?d■	?	?	?d	?	?	?a	3a	?d	?	?	?
Aliphatic and Aromatic Hydrocarbons	?d	2a	2?	?d	?	?	?a	?d‡	?a	2a	?d	?d
Amides and Amines	?	?	?	?	?	?	?	?	3?	?	?	?
Chlorinated Hydrocarbons	?d	2d	2d	?	?	?	?a	?d	?a	2a	?d	?d
Ethers and Epoxides	?	?	?	?	?	?	?a	?	?a	?d	?	?
Heterocyclics	?	?	?	?d	?	?	?a	?	?	?	?	?
Nitriles	?	?	?	?	?	?	?	?	?	?	?	?
Organic Acids and Acid Chlorides	?a	1d	1d	?d	?d	?a	2a	?a	2a	1a	?d	?d
Organometallics	?	?	?	?	?	?	?	?	?	?	?	?
Phenols	?d	1d	?	?d	?d	?	?	2a	?c	?	?	?
Organic Esters	?	?	?	?	?	1a	?	?	?	?	?	?
Inorganic Compounds												
Heavy Metal Salts and Complexes	?d	2c	2a	?d	2c	3?	2?	?	?	?a	?	?
Inorganic Acids	?a§□	1d	1a	?c►	?c	3a	2c	?a§	2c	1d	?a§	?a☆
Inorganic Bases	?a	1a	1a†	?c►	?d	2c	3d	?d	?d	2c	?a	?d
Inorganic Salts	?d	2c	2a	2d	?d*	3?	3d	3a#	?d	?a	?a	?a

KEY: Compatibility Index

Effect on Set Time

1 No significant effect
2 Increase in set time (lengthen or prevent from setting)
3 Decrease in set time

Effect on Durability

a No significant effect
b Increase durability
c Decrease durability (destructive action begins within a short time period)
d Decrease durability (destructive action occurs over a long time period)

* Except sulfates, which are ?c
† Except KoH and NaOH, which are 1d
‡ Low molecular weight polymers only
§ Non-oxidizing
☆ Non-oxidizing, except HF
□ Except concentrated acids
■ Except aldehydes which are 1a
# Except bleaches which are 3d
► For modified bentonites, ?d
? Data Unavailable

One further assumption is made with respect to organic polymer grouts. The reaction of the organic polymer grout and its curing agent is not complete and a quantity of the unreacted polymer will remain. This assumption reflects the fact that even under highly controlled conditions, the stoichiometry of such reactions is ill-defined, and in a field situation, the conditions are not only uncontrolled, but many times are undefined. The unreacted resins will be assumed to be trapped in the polymer matrix with the reactive sites randomly oriented. These resins will appear on the surface as well as the interior of the grouting wall and will be available for reaction with chemicals brought into contact with the surface. A certain amount of migration from the interior to the exterior of the matrix is also expected to take place. Migration is thought to occur slowly, so the possibility of reactions between the grouted structure and the surroundings may continue for an extended period of time. The predicted compatibilities, though, are made for the totally reacted grout and do not take into account exposure of unreacted resins to the various chemicals.

Based on these assumptions, a number of estimates of grout/chemical compatibilities were made for the silicate and organic polymer grouts. The other grout types were not evaluated due to the lack of knowledge of their actual solidification chemistry. Predictions were made only where no data currently exists. The predictions are only indicative based on reaction chemistry. These are the effects a chemical might have on a grout and not the true field effect. These predictions are presented in Figure 7 and are discussed in the following sections.

Silicate Grouts

As discussed in Section 3, silicate grouts are composed of polymetric chains of silicon-oxygen linkages with cations of alkali metals dispersed along the chain and bonded to the oxygen. The alkali metals can be replaced by divalent ions such as calcium and magnesium. The divalent ion permits bonding with two oxygens, thus, a cross-linked polymeric structure is formed (Hurley and Thornburn 1971). Because silica gel is a fairly efficient ion exchanger, a landfill containing a high concentration of soluble salts may cause either one of two effects:

1. Decrease durability by exchanging monovalent ions for divalent ones, thus decreasing the cross-linking

2. Increase durability by exchanging divalent ions for monovalent ones, thus increasing the cross-linking.

Ferric iron is reported to be an inhibitor for silicate grout, stopping or slowing down gelation time. The resultant gel is weak (Office of the Chief of Engineers 1973). The mechanism for the inhibiting effect may be due in part to the tendency of aqueous ferric iron to hydrolyze and/or form complexes (Cotton and Wilkinson 1972) thereby removing or bonding with the water molecules from the grouting mixture.

Figure 7. Predicted Grout Compatibilities

Grout Type / Chemical Group		Polymers					
	Silicate	Acrylamide	Phenolic	Urethane	Urea-formaldehyde	Epoxy	Polyester
Organic Compounds							
Alcohols and Glycols	1a	1 –	3b	–	1?	1 –	1 –
Aldehydes and Ketones	1a	? –	–	1 –	?	1a	1a
Aliphatic and Aromatic Hydrocarbons	1d	1 –	? –	1 –	–	1 –	1 –
Amides and Amines	3a	3d	3b	– a	1a	1a	3a
Chlorinated Hydrocarbons	1d	1 –	? –	1 –	–	1 –	1 –
Ethers and Epoxides	1a	1 –	1a	1 –	? –	1a	1a
Heterocyclics	1d	1 –	1a	1a	1a	1a	1a
Nitriles	1a	3?	1a	1a	1a	1a	1a
Organic Acids and Acid Chlorides	1 –	–	3 –	2 –	–	? –	1 –
Organometallics	1a	3a	?	–	1a	1a	3► ?
Phenols	1a	1a	–	2 –	1a	1a	1?
Organic Esters	–	?	?	?	?	?	1d
Inorganic Compounds							
Heavy Metal Salts and Complexes	– a	– ?	?	3► ?	? –	3?	3?
Inorganic Acids	–	–	2 –	–	–	1 –	1 –
Inorganic Bases	–	–	3 –	? –	–	? –	1 –
Inorganic Salts	– d	–	–	? –	? –	? –	3* –

KEY: Compatibility Index

Effect on Set Time

1 No significant effect
2 Increase in set time (lengthen or prevent from setting)
3 Decrease in set time

Effect on Durability

a No significant effect
b Increase durability
c Decrease durability (destructive action begins within a short time period)
d Decrease durability (destructive action occurs over a long time period)

* If metal salts that are accelerators
► If metal is capable of acting as an accelerator
? Determination of compatibility could not be made based on available information

The presence of organic contaminants has been reported to have the potential for completely preventing the settings of some gels (Hurley and Thornburn 1971). No further details were given. Because each individual organic chemical is present at a concentration of 1% or less, it is assumed that the effect on the set time or durability will be negligible. However, the total concentration of organics may be significant and if the presence of known organic inhibitors such as hydroquinone or accelerators such as alcohols or glycols is sufficiently large, set times and durability may be adversely affected. Catalysts in general are present in mixtures at a 0.1 to 2 percent concentration.

Acrylamide Grouts

Acrylamide grouts, formed by reacting a mixture of two organic monomers with a cross-linking agent are expected to be resistant to the deleterious effects of most organic chemicals. However, other chemicals present during the reaction period that alter the monomer cross-linking agent ratio may result in a weaker, softer grout. The presence of metal ions in the landfill may inhibit setting of acrylamide grout. The activator, triethanolamine, is reported to be metal sensitive (Clarke 1982). Because the gel time is dependent on the concentration of the catalyst, activator-inhibitor any interference with these chemicals will result in a change in the process (Clarke 1982).

The accelerators are reported to be organic compounds such as nitrilotrispropionamide, dimethylaminopropionitrile and triethanolamine. It is expected, therefore, that similar compounds, e.g., nitriles, amides, and amines, present in the landfill at concentrations of 1% will have an accelerating effect on the gel time of the grout. Unreacted monomer trapped in the gel matrix may be expected to react with components in the landfill and these reactions would be characteristic of the reactive site on the molecule, in this case, the amide and the double bond. Amides in general will undergo hydrolysis under either acidic or basic conditions.

Addition to the double bond in the amide is a common reaction and under acidic conditions double bonds undergo hydration to form alcohols. Chlorine and bromine will react with double bonds to form the halogenated compounds in solvents such as carbon tetrachloride. Thus, an organic solvent layer containing halogens in contact with the grout could result in halogenation of the unreacted monomer at the surface. If these reactions result in soluble compounds in either the aqueous or organic layers, the durability of the grout wall may be decreased. This type of reaction would be expected to occur slowly. These reactions may also alter the permeability of the grouted mass in the short term by providing "holes" caused by the solubilization of the reaction products.

Phenolic Grouts

The most common grout in this class results from the polymerization of resorcinol and formaldehyde. In this reaction, the function of the catalyst is to control the pH (Clarke 1982). A pH of slightly above 9 produces the shortest setting time. The most commonly used catalyst is sodium hydroxide but many other materials may function as catalysts (Clarke 1982). In this case, any class of compound that is acidic will contribute to the lengthening of the set time and thus weaken the gel; basic compounds will contribute to a shorter gel time and a stronger gel.

Unreacted monomer contains reactive hydroxyl groups (resorcinol) and an aldehyde group (formaldehyde). Under basic conditions, formaldehyde may react to form methanol and a formate salt. This reaction would result in water soluble products. The solubility of these compounds would be expected to produce a gradual weakening of the grout wall. Contact with organic solvents where carbon tetrachloride is present could result in solubilization of the residual resorcinol, because of its great solubility in that medium. Resorcinol is also soluble in water, alcohol, ether, and acetone (Weast 1972). Formaldehyde is extremely soluble in either an aqueous layer containing acetone or an organic layer containing ether and/or benzene. Thus, prolonged contact with either an aqueous layer containing acetone or an organic layer containing ether and/or benzene could also result in a weakening of the grout by solubilization of the trapped monomers.

Aqueous hydroxides will convert phenols into their respective water soluble phenolic salts. Phenols also form complexes with ferric chloride (Morrison and Boyd 1969).

Urethane Grouts

Urethane grouts are formed from the reaction of isocyanates and polyols where the monomer cross-links with itself. Catalysts are tertiary amines and tin salts. Isocyanate groups will also react with carboxylic groups, hydrogen and nitrogen ions, and water (Clarke 1982). Toluene diisocyanate (TDI) the monomer, will polymerize in the presence of water. Unreacted isocyanate groups trapped in the grout matrix are expected to be available for chemical reaction.

The isocyanate moiety is highly reactive and will react with a host of organic compounds. The aromatic isocyanates in general are more reactive than their aliphatic counterparts (Saunders and Frisch 1962). Because of this reactivity, unreacted isocyanate that is trapped at the surface of the grouted mass may be expected to react with the majority of the substances present in the landfill. If these reaction products are water soluble, a weakening in the grouted structure may occur. For example, the reaction of alcohols with isocyanates produces a class of compounds called carbonates (these are also urethanes) (Saunders and Frisch 1962). The water solubility of these compounds varies from insoluble to very soluble with many being only slightly soluble in water. While it is not possible to generalize an effect of this reaction, the potential exists for extremely soluble reaction products. Additionally, if enough of the isocyanate reacts with the groundwater contaminants, the grout may not set.

Many metallic compounds have been found to be catalysts for the isocyanate-hydroxyl reaction. Examples include: bismith, lead, tin, strong bases, titanium, iron, antimony, uranium, cadmium, aluminum, mercury, zinc, and nickel (Saunders and Frisch 1962). Since many of these metals are commonly found in leachate from landfills, their potential catalytic effect cannot be ignored.

Once the grout has set, the fully reacted species are expected to be resistant to the effects of a great majority of the chemicals found in landfills.

Urea-Formaldehyde Grouts

Urea-formaldehyde grouts will set up only under acidic conditions (Clarke 1982). Once properly formed, the urea- formaldehyde grouts are impervious to most chemicals. However, free formaldelyde is usually present to some degree in the grout matrix and surface contact may result in a leaching of the free formaldehyde by the aqueous media, since formaldehyde is quite soluble in water. The presence of methanol enhances the solubility of formaldehyde in water (Meyer 1979). The leaching of formaldehyde from the matrix surface may result in a migration of free formaldehyde from the interior matrix to the surface and a gradual weakening of the grout.

Epoxy Resin Grouts

The most important raw materials for epoxy resins are epichlorohydrin and bisphenol-A. These chemicals are reacted in the presence of a caustic soda solution, generally with a large excess of epichlorohydrin. This excess produces epoxide-terminated resin molecules (Scheldknecht and Skeist 1977). Prior to injection, the resin is then cross-linked with either reactive curing agents, such as tertiary amines combined with reactive primary and secondary amines, or through homopolymerization by use of catalysts (Scheldknecht and Sheist 1977). The epoxy resins are soluble in ketones, esters, and glycol ethers which are used as diluents. Aromatic hydrocarbons and alcohols are sufficiently compatible to also function as diluents. Reactive diluents such as butyl glycidyl ether, cresyl glycidyl ether, phenyl glycidyl ether, and styrene oxide decrease viscosity but also reduce the cross-linking. Thus, the water resistance of the polymer is lowered somewhat (Scheldknecht and Sheist 1977).

The chemical resistance of epoxy grouts is, with the exception of oxidizing acids, reported to be excellent (Scheldknecht and Sheist 1977). It would appear, therefore, that uncured resin trapped in the cross-linked matrix would be subject to the solubilization effects of ketones, esters, ethers, aromatic hydrocarbons, and alcohols.

The curing of epoxy resins is reported to be accelerated by metallic driers such as cobalt naphthenate (Scheldknecht and Sheist 1977). Therefore, any metallic driers or similar compounds present in the landfill have the potential to accelerate the curing process.

Polyester Resin and Grouts

Polyester resins are condensation products of unsaturated diacids and dialcohols. Because these products are quite viscous, they are often mixed with a diluent such as styrene. The polymerization process is catalyzed by a peroxide which generates free radicals in the presence of an accelerator such as cobalt, manganese, and vanadium salts; tertiary amines; mercaptans; or quaternary ammonium salts (Tallard and Caron 1977a). Once polymerized, the grout would be expected to be relatively impervious to most components of a landfill.

However, during the polymerization process, the presence of excess accelerator as components of landfill leachates may have an adverse effect on the grout by decreasing the set time. The polymerization process normally gives off considerable amounts of heat and if this process were speeded up, more heat would be generated (Tallard and Caron 1977a). In such cases, the heat would be transferred to the immediate surrounding area. Since many chemical reactions are enhanced in the presence of heat, the unreacted components of the grouting mixture may undergo reactions with chemicals in the leachate rather than continue the polymerization process. For example, depending upon the temperatures generated, halogen additions to the double bond of any of the components of the grouting mixture may occur. Water may also add to the double bonds, forming alcohols. The diluent, styrene, may dimerize instead of co-polymerizing with the reactants. In such cases, the formation of the simple ester may not be inhibited, but the polyester formation may be inhibited by competitive reactions, or the final polymer may be altered in structure because other parts of the molecule (i.e., the double bonds) may have reacted with components of the leachate. In such cases, the durability of the grout is unpredictable, and thus it may be inadvisable to use.

SECTION 7

GROUT COMPATIBILITY TESTING PROCEDURES

In order to establish the compatibility of compounds contained in groundwater with the materials used in the grouting, a series of laboratory tests must be performed. The two grout properties that must be investigated are the permeability of the grouted mass, and the set time of grout in the contaminated environment. There are as yet no established procedures for determining the effect that various chemicals would have on these characteristics. An evaluation of currently utilized grout and soil test methods, however, has identified several potential procedures.

The following sections outline the testing procedures that are applicable to determining grout/chemical compatibility.

PERMEABILITY OF GROUTED SAND

The effect that leachate will have on the ability of a grouted mass to contain leachate can be measured in the laboratory. By bringing chemicals at representative concentration levels into contact with a sample of the grouted material within a permeameter, their rate of movement through the grouted sample can be measured. By comparing this rate with that obtained with water, the change in permeability can be determined.

Laboratory determinations of permeability are based on Darcy's Law. This expression relates the flow of a liquid through a porous medium with the hydraulic gradient, permeability, and cross-sectional area of the flow, as follows (Spangler and Handy 1973):

$$Q = kiA$$

where:

Q = flow rate (units: $[\text{length}]^3/\text{time}$)
i = hydraulic gradient
A = cross-sectional area of the flow
k = coefficient of permeability (units: length/time)

In order to calculate the coefficient of permeability (k) in the laboratory, Q, i, and A are measured. The coefficient of permeability (often termed permeability) will depend on the size and shape of the soil grains, the void ratio of the sample, the shape and arrangement of the voids, and the sample saturation (Office of the Chief of Engineers 1970).

Permeability computed on the basis of Darcy's Law is limited to conditions of laminar flow and complete saturation of the voids. Under turbulent flow conditions, the flow is no longer proportional to the first power of the hydraulic gradient. Under conditions of incomplete saturation, the flow is in a transient state and is time dependent (Office of the Chief of Engineers 1970). Thus, all permeability testing procedures must be carried out under the Darcy conditions of flow.

There are a number of permeability test methods that have been developed for use in low permeability soils and/or grouted samples. These methods have been used to determined the effect of leachate on soil or soil bentonite mixtures. These methods, and the sample preparation procedures used, are discussed in the following subsections.

Permeameters

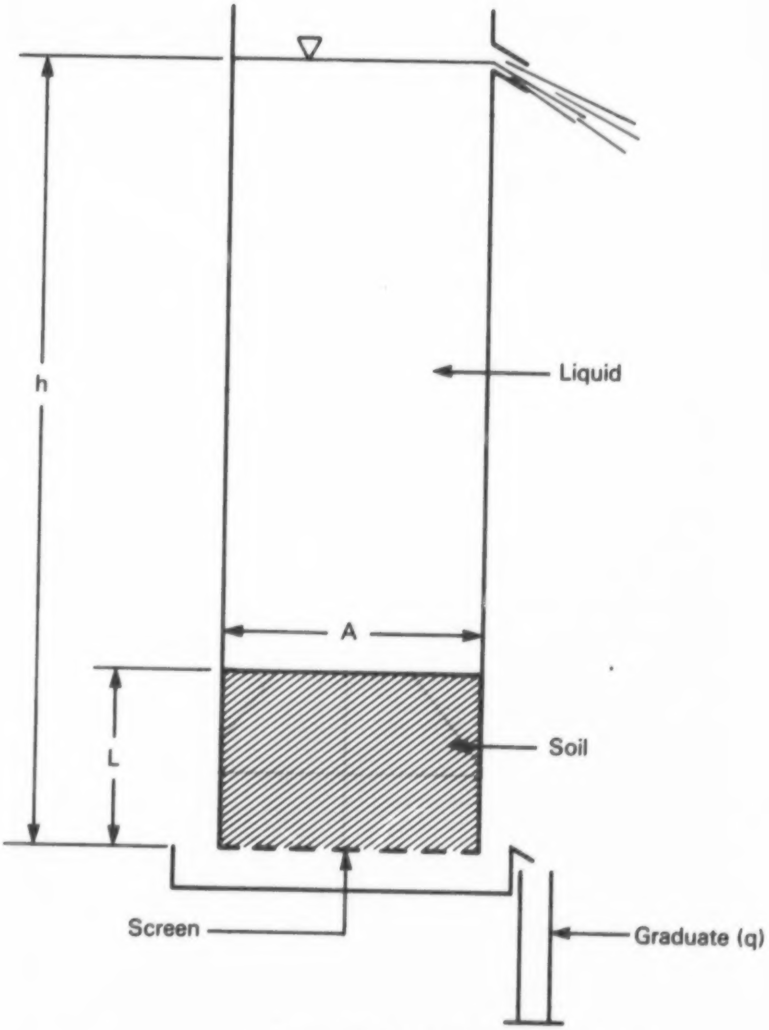
To measure permeability in the laboratory while observing the limits established by Darcy's Law, two types of tests have been developed: constant-head and variable head. These tests can be performed by a variety of testing equipment, depending on the samples characteristics. The three basic categories of test equipment are as follows:

- Fixed wall permeameter cells
- Triaxial permeameter cells
- Consolidation permeameter cells (Office of the Chief of Engineers 1970).

Permeability tests on samples with low permeability, such as grouted formations, must be performed carefully if they are to be accurate. Leaks, losses of volatiles, or channelized flow between the permeameter and the sample can greatly effect permeability values (Anderson and Brown 1981). The following sections outline test procedures and equipment that have been developed to overcome these potential problems as well as the limitations of each procedure.

Permeability Tests: Constant Head and Variable Head--

The difference between these types of permeability tests, constant head and variable head, is the way in which the amount of liquid that flows through the sample is measured; thus the procedures used for calculating permeability are different. For example, in the constant head test, the hydraulic gradient "i" is held constant throughout the test. Figure 8 illustrates a simple constant head permeameter.


h
Liquid
A
L
Soil
Screen
Graduate (q)

Source: Office of the Chief of Engineers, 1970

Figure 8. Constant Head Permeameter

By utilizing a variation of Darcy's Law, permeability can be calculated as follows:

$$k = \frac{qL}{hAt}$$

where:

k = coefficient
q = quantity of flow
L = length of sample
h = head of liquid
A = cross-sectional area of sample
t = time interval of test (Office of the Chief of Engineers 1970).

This type of test is usually used for determining permeability in only coarse grained soils with a k value of greater than 10^{-3} cm/sec because of the small heads that can be applied (unless excess pressure is applied through the use of compressed gases) (Office of the Chief of Engineers 1970, Olson and Daniel 1981). The major advantages of this type of test are the simplicity of data interpretation, and the fact that the use of a constant head minimizes confusion due to the changing volume of air filled voids when the soil is not saturated (Olson and Daniel 1981).

For samples with a lower permeability, a variable head test is usually used (Spangler and Handy 1973). In this procedure, the head is allowed to decrease over the course of test as liquid moves through the sample. Figure 9 illustrates a simple variable head test apparatus. The permeability of the sample is calculated from the following variation of Darcy's Law:

$$k = \frac{L}{t} \ln \frac{h_o}{h_f}$$

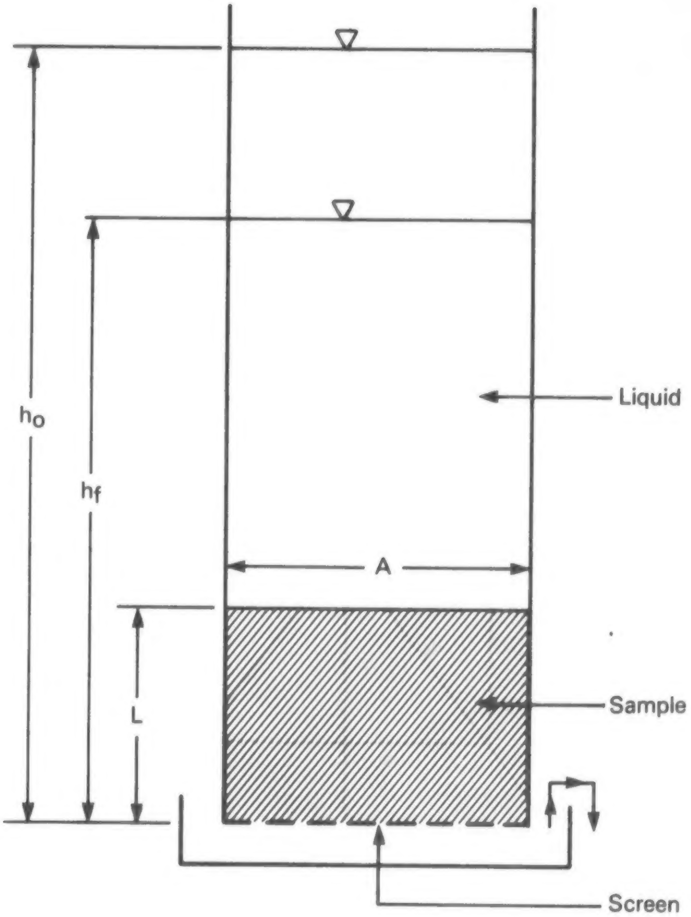
where:

L = length of sample
t = time interval of test
h_o = height of liquid in the standpipe at the beginning of the test

h_f = height of liquid in the standpipe at the end of the test.

This test procedure is usually used on fine grained samples with k values less than 10^{-3} cm/sec (Office of the Chief of Engineers 1970). The advantage of this test is that small flows can be measured more easily (Spangler and Handy 1973).

To reduce the time necessary to run these tests, the flow rates can be increased by superimposing a gas pressure (such as air) on top of the liquid.


h$_o$
h$_f$
L
A
Liquid
Sample
Screen

Source: Office of the Chief of Engineers, 1970

Figure 9. Variable Head Permeameter

A pressure of 4-5 pounds per square inch (psi) is commonly utilized for soil permeability testing while up to 40 psi can be used for grouted soils.*[+][o] While this can significantly reduce the time that these tests take, it can also present several potential problems. At elevated pressures, the liquid can become saturated with the gas in accordance with Henry's Law (Olson and Daniel 1981). Thus, as the liquid flows through the sample and the pressure drops, there may be a tendency for gas bubbles to develop in the sample. This can have a significant effect on the sample's permeability. Also, when using gas pressure in the variable head test, a point is reached where the gas pressure will be significantly higher than the pressure due to the liquid, and the test becomes just a constant head test.

Fixed Wall Permeameter Cells--

Fixed-wall permeameter cells are the simplest type of permeameters that can be utilized. In this type of permeameter, the sample is contained in a fixed wall cylinder supported by a porous disk or screen. To prevent swelling of the sample, a plate can be clamped against the sample's upper surface (Office of the Chief of Engineers 1970, Olson and Daniel 1981). This apparatus can be either a constant head or variable head system as illustrated in Figure 10. The advantage of this technique is that the apparatus is readily available and easy to use. The disadvantage is that improper placement of the sample in the permeameter can cause leakage between the sample and the permeameter wall. This will invalidate any measurements made with the sample (Zimmie 1981). General procedures for performing this test can be found in Appendix VII of Laboratory Soils Testing (Office of the Chief of Engineers 1970). This type of permeameter has been used by Northwestern University to measure permeability of grouted sand samples. In these tests, the permeameter cell was the mold in which the sand sample was grouted. This approach eliminates problems that could result from mishandling of the sample during its removal from the mold and insertion into a permeameter.

The American Petroleum Institute (API) also recommends the use of a fixed wall permeameter to test the permeability of cement (API 1982). In this test, the sample is first saturated by drawing water through it with a vacuum. A pressure of 200 psi is then applied to the feed solution and a backpressure of 20 psi is applied to the solution that has permeated the sample. This results in an effective pressure of 180 psi being utilized to force the feed solution through the sample.

Consolidation Permeameter Cells--

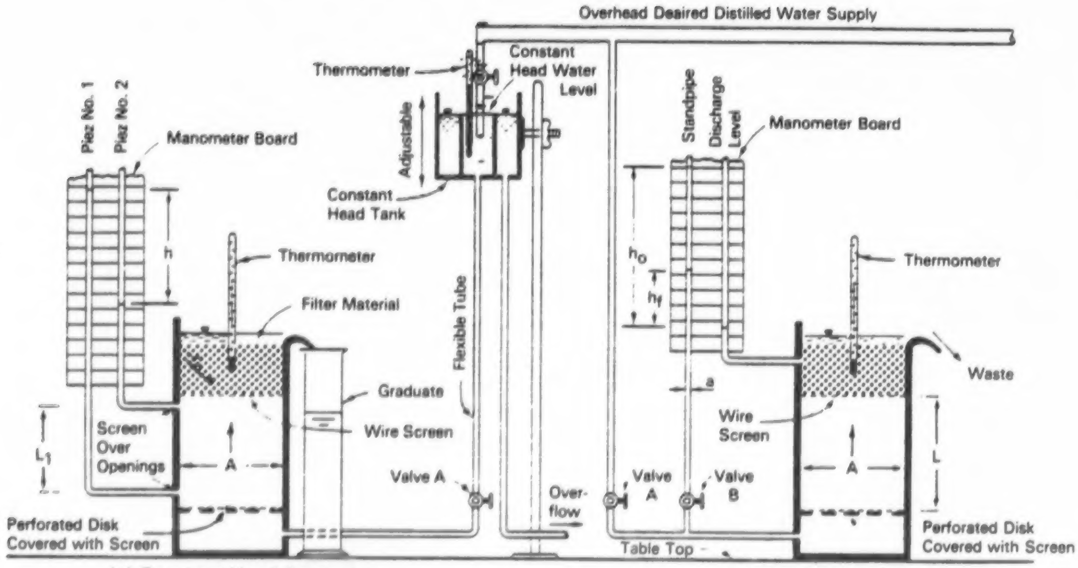
Consolidation permeameter cells are similar to fixed wall cells except a load can be placed onto the top of the sample (see Figure 11). The load

---

*Hale, G. USAE Waterways Experimental Station, Vicksburg, MS. Personal communication with G. Hunt, August 30, 1982.

[+] Ayers, J. GZA Corp, Newton Upper Falls, MA. Personal communication with G. Hunt, September 3, 1982.

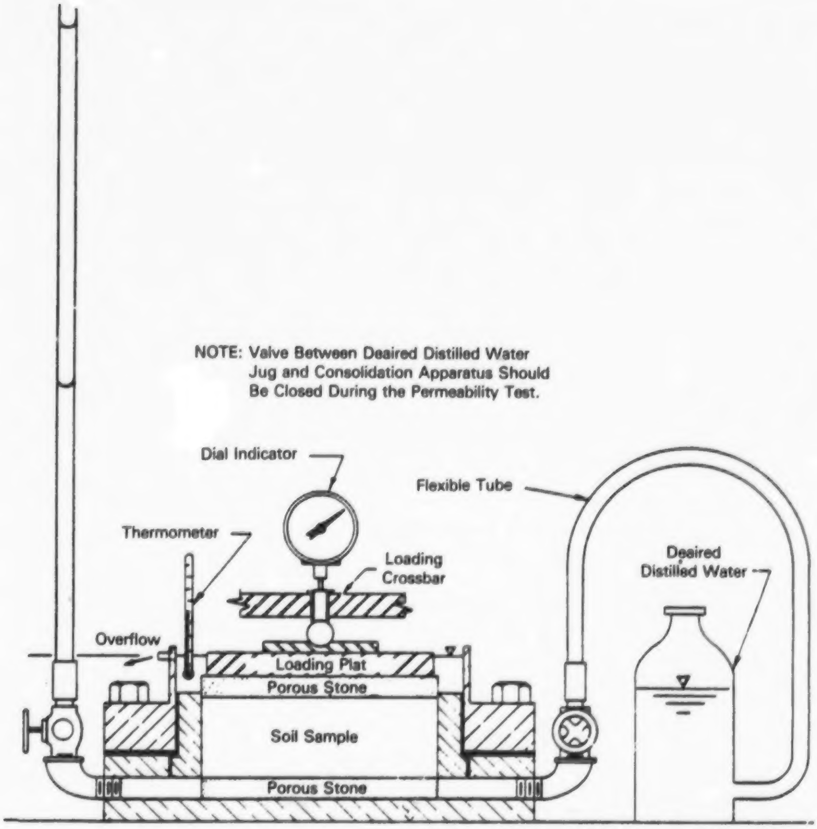
[o] Krizek, R. Northwestern University, Chicago, IL. Personal communication with G. Hunt, October 11, 1982.


Overhead Desired Distilled Water Supply
Thermometer
Constant
Head Water
Level
Adjustable
Constant
Head Tank
Piez No. 1
Piez No. 2
Manometer Board
h
Thermometer
Filter Material
Flexible Tube
Graduate
Wire Screen
Screen
Over
Openings
L_1
A
Valve A
Over-
flow
Perforated Disk
Covered with Screen
Standpipe
Discharge
Level
Manometer Board
h_o
h_f
Thermometer
Waste
a
Wire
Screen
A
L
Valve
A
Valve
B
Table Top
Perforated Disk
Covered with Screen

(a) Constant-Head Apparatus **(b) Variable-Head Apparatus**

Source: Office of the Chief of Engineers, 1970

Figure 10. Constant-Heat and Variable Head Permeameters


NOTE: Valve Between Deaired Distilled Water
Jug and Consolidation Apparatus Should
Be Closed During the Permeability Test.
Dial Indicator
Flexible Tube
Thermometer
Loading
Crossbar
Deaired
Distilled Water
Overflow
Loading Plat
Porous Stone
Soil Sample
Porous Stone

Source: Office of the Chief of Engineers, 1970

Figure 11. Variable Head Consolidation Permeameter

placed upon the sample will cause an effective seal to be formed between the sample and the walls of the permeameter. This test is best used for undisturbed soil samples. With this type of apparatus, permeabilities as low as 10^{-12} cm/sec have been measured (Olson and Daniel 1981).

Procedures for performing this test can be found in Appendix VII of Laboratory Soils Testing (Office of the Chief of Engineers 1970).

Triaxial Permeameter Cells--

In a triaxial permeameter cell, a cylindrical sample is confined in a rubber membrane and subjected to an external hydrostatic pressure during the permeability test. This prevents leaks and sideflow along the sides of the specimen (Zimmie 1981, Office of the Chief of Engineers 1970). An example of this type of permeameter is shown in Figure 12.

Another advantage of this system is that through an increase in pressure on the sample, gas bubbles contained within the sample can be dissolved in the pore fluid, thus leaving the sample totally saturated. This is accomplished by simultaneously increasing the chamber pressure and the pressure on the pore fluid, while maintaining the same effective stress on the sample (Zimmie 1981). The pressure applied to the pore fluid is known as the backpressure and is typically about 40 psi* for soil samples.

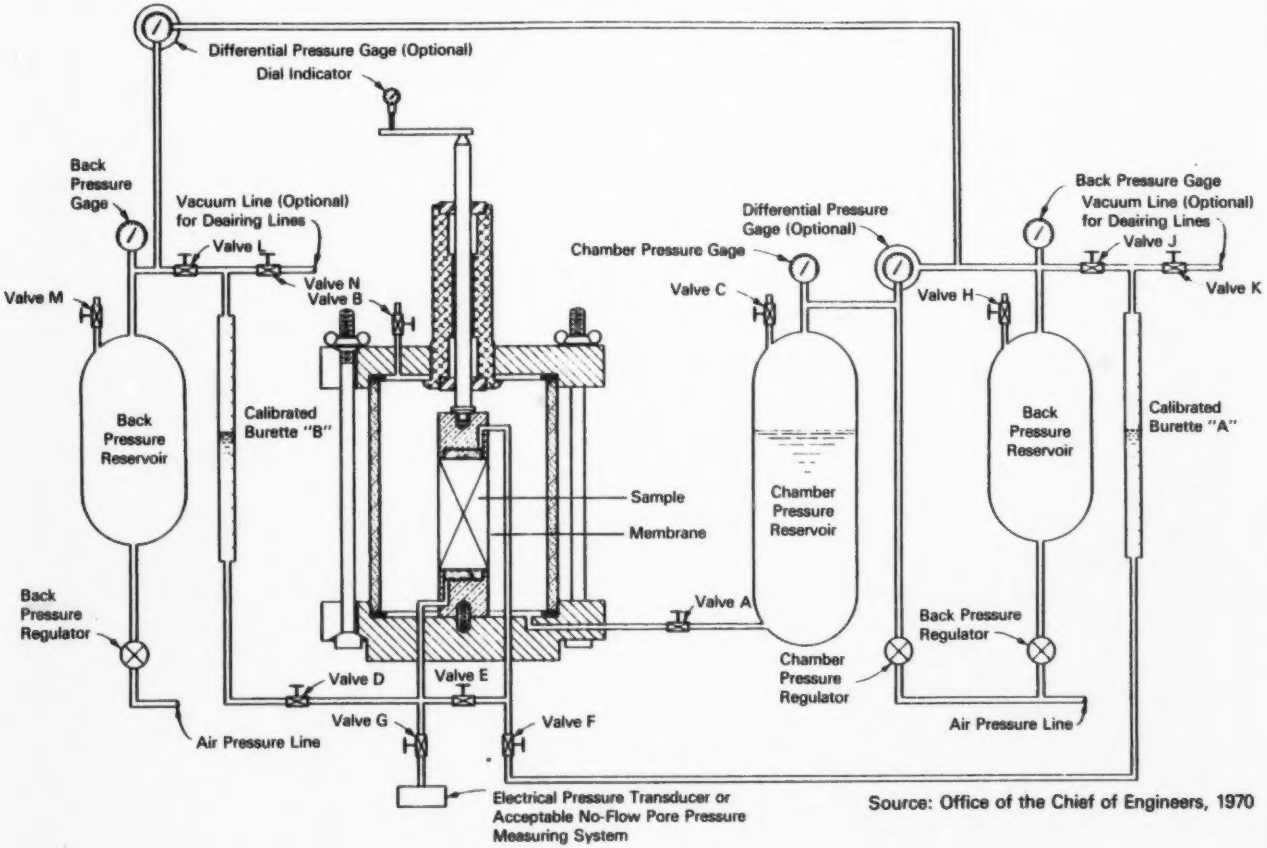
The advantages of using this type of permeameter are that it greatly reduces the chance of liquid flow around the sample, and allows for complete saturation of the sample. The disadvantage is that it is a relatively complex procedure requiring expensive equipment. Several laboratories recommended the use of triaxial permeameters because of their ability to reduce short circuiting of the leachate*[+].

It should be noted that backpressure does not have to be utilized in performing triaxial permeability tests. Tallard and Caron (1977b) utilized a modified triaxial permeameter to deterime the permeability of grouted sand (see Figure 13). In this system, the grouted sand sample is covered with a latex membrane and placed in the permeameter. Water, under a pressure of 14 psi, is then drawn through the sample by a vacuum. When the water has saturated the sample, the vacuum is released and the test is run with a confining pressure of 21.8 psi on the membrane. This system has been utilized to study a wide range of grouts including silicates, lignochromes, polyacrylamides, phenoplasts, and bentonite.

---

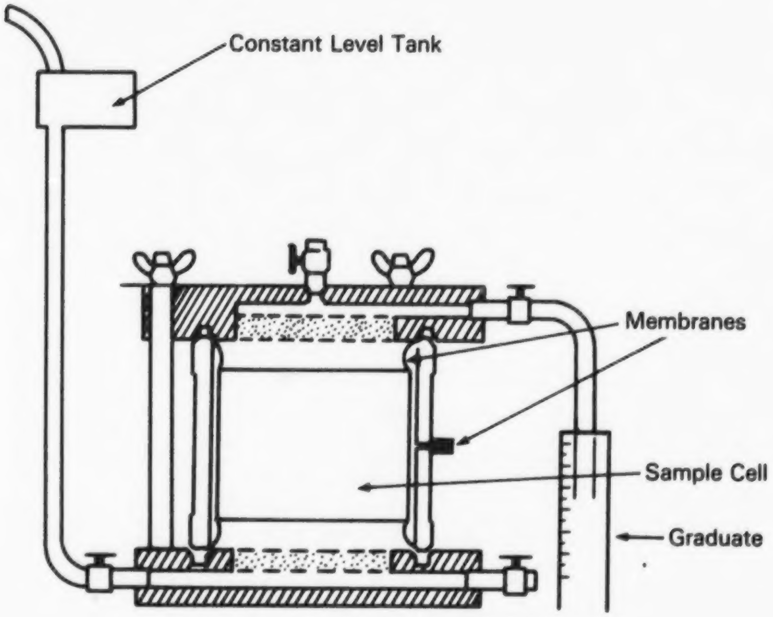
*Schwartz, G. ECI, Pittsburgh, PA. Personal communication with G. Hunt, August 20, 1982.

[+] Hentz, D. Federal Bentonite Belle Fourche, SD. Personal communication with G. Hunt, August 19, 1982.


Differential Pressure Gage (Optional)
Dial Indicator
Back Pressure Gage
Vacuum Line (Optional) for Deairing Lines
Valve L
Valve N
Valve B
Valve M
Back Pressure Reservoir
Calibrated Burette "B"
Sample
Membrane
Back Pressure Regulator
Valve D
Valve E
Valve G
Valve F
Air Pressure Line
Electrical Pressure Transducer or Acceptable No-Flow Pore Pressure Measuring System
Chamber Pressure Gage
Valve C
Differential Pressure Gage (Optional)
Valve A
Chamber Pressure Reservoir
Chamber Pressure Regulator
Valve H
Back Pressure Gage
Vacuum Line (Optional) for Deairing Lines
Valve J
Valve K
Back Pressure Reservoir
Back Pressure Regulator
Air Pressure Line
Calibrated Burette "A"

Source: Office of the Chief of Engineers, 1970

Figure 12. Triaxial Permeameter with Back Pressure


Constant Level Tank
Membranes
Sample Cell
Graduate

Source: Tallard and Caron, 1977b

Figure 13. Constant Head Triaxial Permeameter

Potential Problems Presented by Permeability Tests--

There are several sources of error associated with laboratory permeability tests that can affect the accuracy of the results. These include:

- Incomplete initial saturation of the test sample, or accumulation of gas bubbles with the sample. This can greatly reduce the measured permeability.
- Leakage around the sides of the sample can significantly affect the measured permeability.
- Changes in the temperature of low permeability samples in long term tests can affect the measured permeability (Office of the Chief of Engineers 1970, Olson and Daniel 1981).

While all permeability tests can be affected by a number of problems, the evaluation of a particular permeameter test hinges not so much on the types of equipment utilized, but the test and quality control procedures followed during the study. The preliminary results of an on-going study show that the use of fixed wall or triaxial devices will not affect the results of the permeability tests of a soil/bentonite mixture.* Thus, more attention should be paid to the test procedures than to the type of equipment used.

Grout Sample Preparation

The grout to be tested must be first mixed with a material that resembles soil. Since an inert, well defined material that is easy to mix with grout is needed, sand is usually used. Tallard and Caron (1977b) recommend sand with a gradation from 0.1 to 0.3 mm. Other studies have used sands with well-defined size ranges including Ottawa 20-30 sand (Borden, Krizek, and Baker 1982), Number 20 Monterey sand (Vinson and Mitchell 1972), and Number 20 and 16 Monterey sand (Clough, et al. 1977).

While the sand can be mixed with the grout in a beaker, the best results are obtained when the grout is injected into the sand contained within a mold or column (Tallard and Caron 1977b). Although there is no current method established for preparing the grouted sand sample, an ASTM procedure has been proposed which outlines the packing and injection procedures for preparing a chemically grouted sand specimen. This procedure basically consists of placing the sand in a split mold at the desired density and injecting the sand with grout (Baker 1982).

Various studies have developed procedures for packing the sand into the container and injecting the grout into the sand. The apparatus in which the sand is contained can be a column, fixed-wall permeameter cell, or mold such as a California Bearing Ration (CBR) mold* (Vinson and Mitchell 1972, Tallard and Caron 1977b, Clough et al. 1977, Johnson 1979). Tallard and Caron (1977b) give detailed directions as to what size column should be used, how the sand should be packed into the column, under what pressure the grout should be injected, and how long the grout should be cured. Another study (Clough et al. 1977) utilized an apparatus which allowed water to first be injected into the columns, followed by the grout (see Figure 14).

---

*Ayers, I. GZA Corp., Newton Upper Falls, MA. Personal communication with G. Hunt, September 2, 1982.

The container of sand into which the grout is injected should contain the fluid, either water or leachate, that the grout must withstand. Once injected, the grout should be allowed to cure for a specific period of time before it is used in a permeability test. The cure should be under wet conditions in order to simulate those found in the field.

EFFECT OF LEACHATE ON GROUT SET TIME

The moment at which a grout sets can be expressed as a specific point in the evaluations of a property characteristic of the grout. Some of these could be:

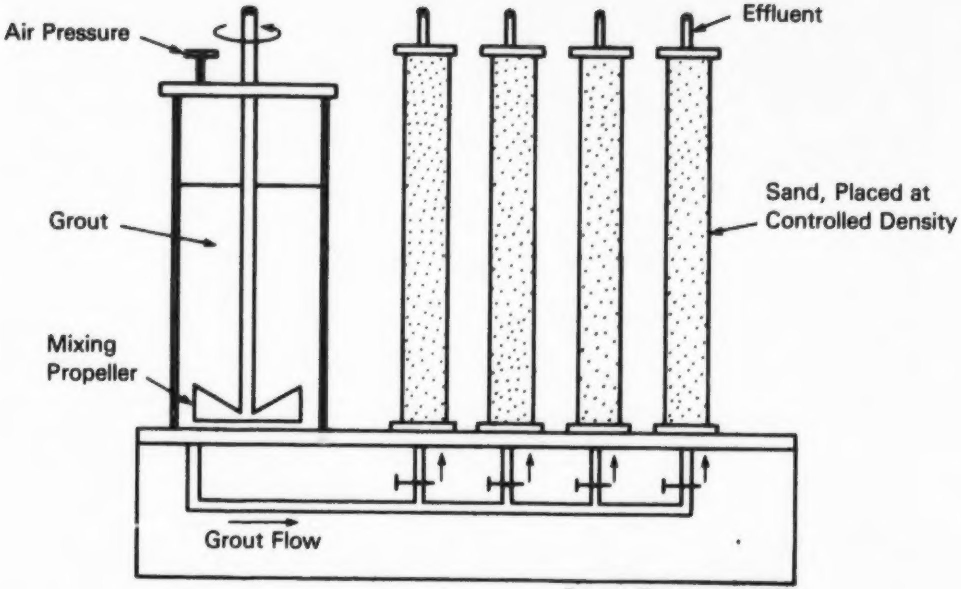
- Rheological - viscosity, rigidity, shear limit
- Mechanical - compression strength, shear strength
- Thermal - critical temperature
- Optical - nephelometry
- Physio-chemical - pH, conductivity, electrical potential for reducing oxides
- Physical - solubility, surface tension (Tallard and Caron 1977b).

Unfortunately, there is no one property that can be used for all grouts to indicate when they have set (Tallard and Caron 1977b). The simplest method, applicable to most grouts (except bituminous emulsions), is the interval of time after which the grout can no longer be transferred from one container to another (Tallard and Caron 1977b). This method of observation, while somewhat subjective, can give a fairly accurate measurement of the setting time for most chemical grouts.*

Setting time in the field is usually determined when the required injection pressure increases noticeably. This measurement is unfortunately not applicable to laboratory scale tests. In small test containers the grout will not set while injection pressure is still being applied. Thus, the set

---

*Krizek, R. Northwestern University, Chicago, IL. Personal communication with G. Hunt, October 11, 1982.


Air Pressure
Effluent
Grout
Sand, Placed at Controlled Density
Mixing Propeller
Grout Flow

Source: Clough et al., 1977

Figure 14. Schematic of Grouting Test Apparatus

time can be artificially extended to periods longer than would actually be encountered in the field, or as indicated by other laboratory measurements.+

A number of devices have been utilized that will give quantitative measurements of setting time by measuring changes in viscosity with time. The viscosity of a grout will increase with time until some point is reached at which it is deemed set. This relationship can vary depending on the type of grout utilized. The viscosity of silicate grouts will slowly increase with time until a rapid gelation takes place. Acrylamide grouts stay at about the initial viscosity until a rapid change in viscosity takes place indicating set (Clarke 1982). Clays, on the other hand, will show a steady increase in viscosity with time, with no point of rapid viscosity change (Tallard and Caron 1977b). The set time for clays, then, can be determined when a pre-selected viscosity is reached.

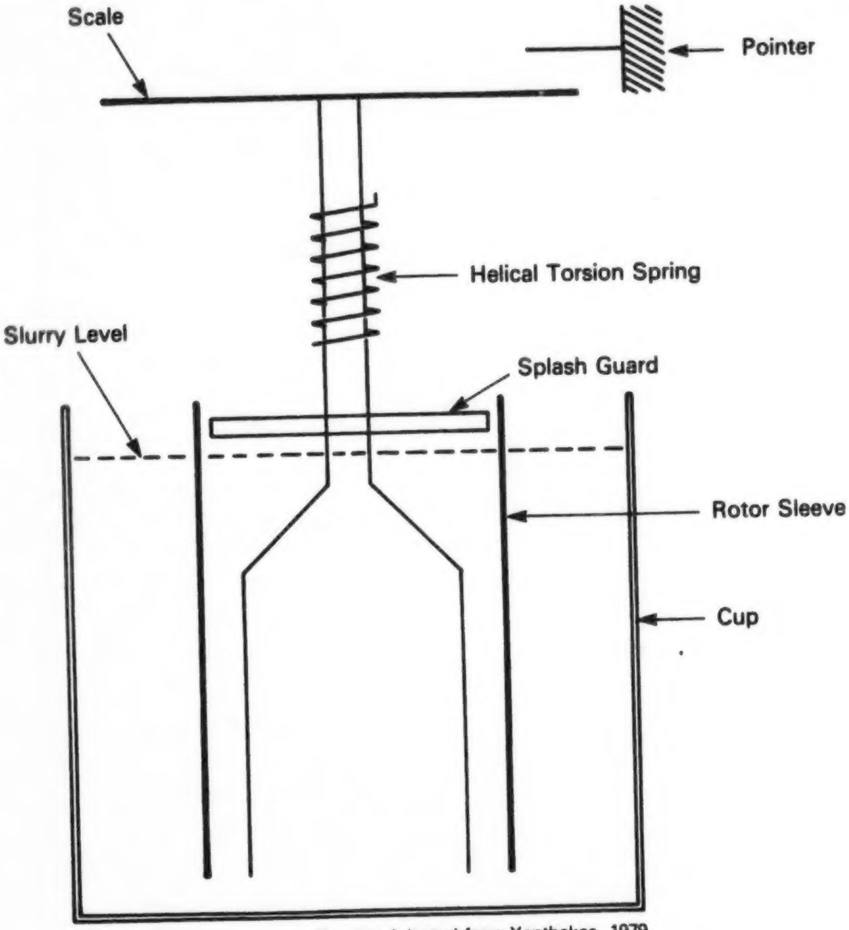
For chemical grouts, a Brookfield Viscometer can be utilized to measure the change in viscosity. This method is outlined in ASTM Standard D4016-81: Standard Test Method for Viscosity of Chemical Grouts by Brookfield Viscometer. The change in viscosity with time can also be determined for most grout types by a direct indicating viscometer, known as a Fann Viscometer (Tallard and Caron 1977b). In this device the slurry is sheared between two cylinders. The shear stress is derived from the torque on one of the cylinders, while the average rate of shear is estimated from the measured rate of rotation and the diameters of the two cylinders, as illustrated in Figure 15 (Xanthakos 1979). The procedures for performing this test and the required calculations are outlined in Standard Procedures for Testing Drilling Fluids, API RP13B. API has also established procedures for measuring the thickening time of cement using a consistometer. This device relates the torsion of a paddle rotating in a slurry to degrees of firmness. The procedures for performing this test can be found in API Specification 10: API Specification for Materials and Testing for Well Cements.

All of the methods discussed so far relate only to measuring the setting time of the pure grout. The setting time in a sand/grout mixture is also important. The gelation can be determined through variations in the mechanical strength properties, such as compression or tension and shear of the sand/grout mixture. The problem in measuring these properties is that the gelation that occurs in the early stages is very weak and difficult to distinguish from the natural cohesion of sand saturated with a viscous liquid (Tallard and Caron 1977b). Also, the sand/grout mixture must be removed from its container in order for the tests to be run. This could prove to be difficult in the early stages of gelation.

In all cases where the setting time is being measured, the chemicals in question should be mixed with the grout to determine their effects. In the case of pure grouts, they can be mixed into the grout. Where grout is injected into sand, the sand can be saturated with the chemical. By

---

+Ayers, J. GZA Corp., Upper Newton Falls, MA. Personal communication with G. Hunt, September 3, 1982.


Scale
Pointer
Helical Torsion Spring
Slurry Level
Splash Guard
Rotor Sleeve
Cup

Source: Adapted from Xanthakos, 1979

Figure 15. Rotational Viscometer

comparing the effect of mixing the grout with pure water or the chemical, their effect on set time can be determined.

OVERVIEW OF COMPATIBILITY TESTS

Unfortunately, there are no established procedures identified in the literature for determining grout/chemical compatabilities. However, there has been a lot of current research done on the effects of chemicals on the permeability of clays and bentonite-soil mixtures (Anderson, Brown, and Green 1982, D'Appolonia and Ryan 1979, D'Appolonia 1980a). The procedures utilized in these studies are applicable to the types of compatibility tests that must be performed on grouts. Though the type of permeability apparatus utilized is not critical, strict quality control procedures must be utilized in running the studies.

For determining the effect of chemicals on set time, there are no procedures that could be readily utilized on all types of grouts. While visual observation of the grout is the easiest way of determining set time, it is not applicable to all grouts and is somewhat subjective. This is an area where more research must be done in order to develop a quantitative method for determining set time.

SECTION 8

GROUT SELECTION

The success of a grouting operation will depend on the selection of the proper grouting materials for the specific area to be treated. Thus the properties of the grout must be matched with the hydrogeological and geological properties of the area to be grouted. This can be accomplished by a step-wise analysis of three basic grout properties:

- Injectability
- Strength
- Durability.

In addition to these properties, other factors such as cost and toxicity, not directly related to the geological setting, should also be considered. In some cases these may be the controlling factors.

By comparing each property to the conditions present in the geological structure, the proper type of grout can be selected. The steps in this selection process are illustrated in Figure 16. The selection of a specific formulation for field application though, requires the assistance of experts in the grouting field. (Tiedemann and Graver 1982).

These properties as they apply to the selection of a proper grout type are discussed in the following subsections. A more detailed discussion of relevant grout properties can be found in Section 5.

INJECTABILITY

The injectability of a grout is controlled either by its viscosity or particle size. This property will dictate the grout's ability to penetrate a soil/rock structure. The lower the viscosity, the finer the voids that can be penetrated. Also, the smaller the particle size in suspension grouts, the smaller the voids that can be penetrated.

For all grouts, the closer the viscosity is to that of water (1.0 cP), the greater the penetration power. (Tiedemann and Graver 1982). Grouts with a viscosity less than 2 cP, such as many of the chemical grouts, can penetrate strata with permeabilities less than 10^{-5} cm/sec. Higher viscosity grouts, like particulate and some chemical grouts with a viscosity greater than 10 cP, can only penetrate coarse strata having permeabilities greater than 10^{-2} cm/sec (Sommerer and Kitchens 1980).

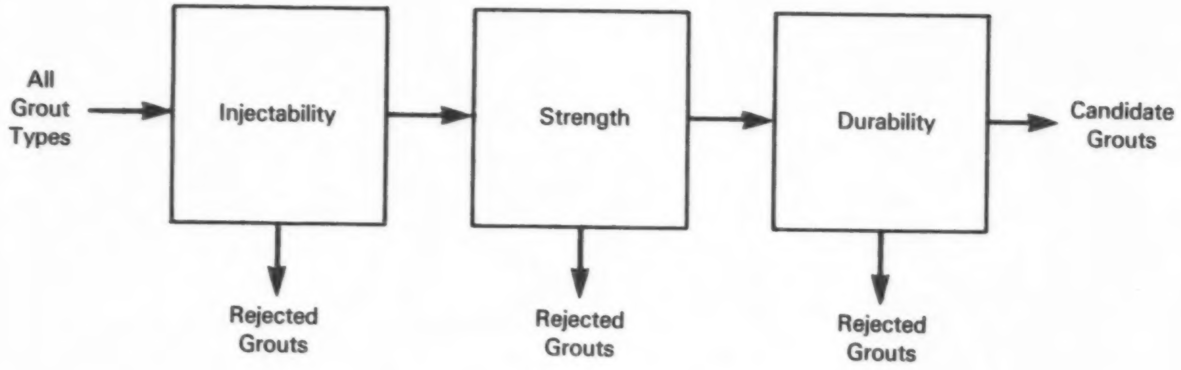

All
Grout
Types
Injectability
Strength
Durability
Candidate
Grouts
Rejected
Grouts
Rejected
Grouts
Rejected
Grouts

Figure 16. Grout Selection Process

For suspension grouts, the particle size will also influence the ability to penetrate voids. A general rule of thumb for determining grout penetrability is sometimes used, which equates grain size of the particles within the grout to soil particles within the stratum. This relationship is:

$$\frac{D_{15}}{D_{85}}$$

where: D_{15} = diameter of grains in the stratum where 15% of the soil mass is finer

D_{85} = diameter of particles within the grout where 85% of the particles is finer

This ratio should be at least 19 and preferably greater than 24 to insure adequate penetration of grout into soil voids (Guertin and McTigue 1982).

Based on these factors, Figure 17 illustrates the type of grout that can be utilized based on the grain size of the stratum. By utilizing this table, grouts that can be injected at a specific site can be identified.

STRENGTH

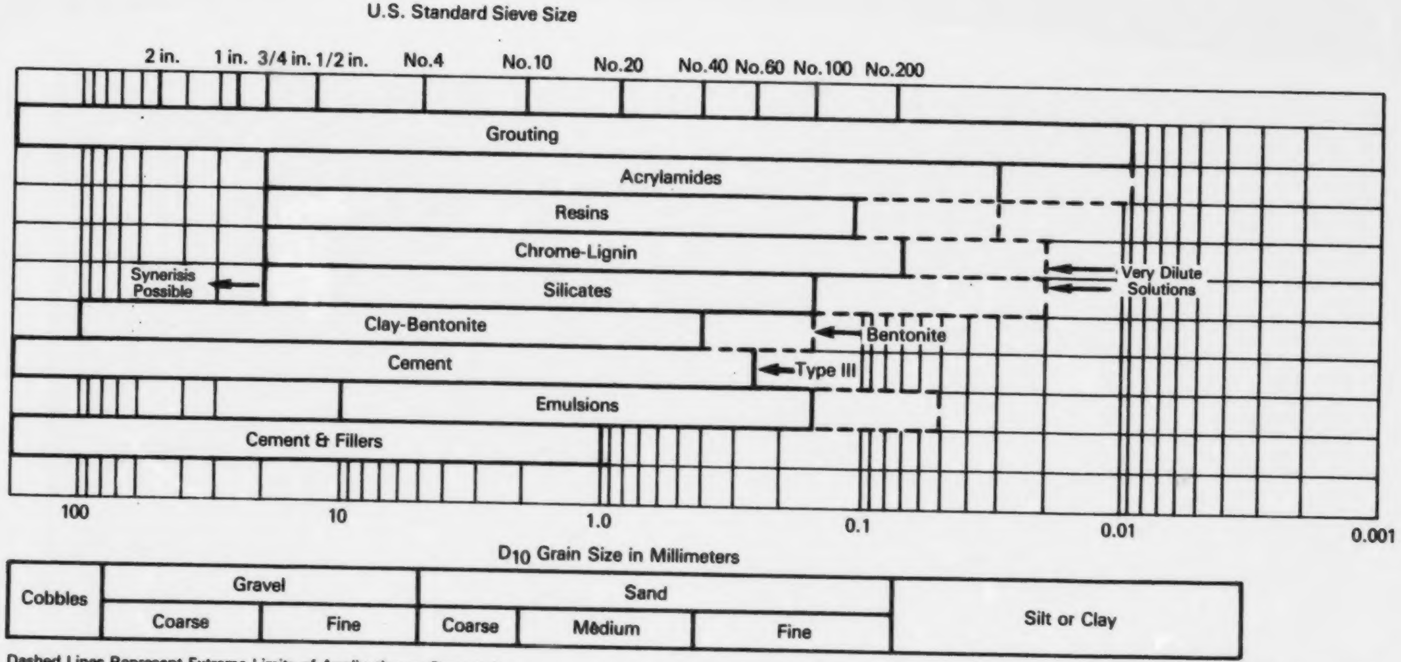
Once a grout has set in the voids in the ground, it must be able to resist hydrostatic forces in the pores that would tend to displace it (Tallard and Caron 1977b). This ability will depend on the mechanical strength of the grout and can be estimated by the grout's shear strength (Tallard and Caron 1977b).

The shear strength of a grout will depend not only on its class, but also on its formulation. Thus, a class of grouts, such as silicates, can possess a wide range of mechanical strengths depending on the concentration and type of chemicals used in its formulation. The strength of the gel, then, can be adjusted, within limits, to the specific situation. Examples of the ranges of shear strengths for several classes of grouts are shown in Table 9.

DURABILITY

For permanent control of groundwater or leachate movement, the grout must not deteriorate with the influence of the soil or groundwater chemistry. Therefore, in the selection process the short and long term durability of the grout must be evaluated.

Deterioration of a grouted area over time can occur through several physical/chemical mechanisms. The grout can be dissolved or structurally changed by water or chemical action. Also, removal of water from the grout through dessication or syneresis can lead to shrinkage of the grout. These factors can weaken a grout, leading to increased permeability (Tallard and Caron 1977b, Sommerer and Kitchens 1980).



Dashed Lines Represent Extreme Limits of Application as Reported in the Literature; Solid Lines Apply to More Typical Applications

Source: Guertin and McTigue 1982

Figure 17. Applicability of Different Classes of Grouts Based on Soil Grain Size

TABLE 9. RANGES OF VALUES OF VARIOUS PROPERTIES OF SELECTED GROUT TYPES

GROUT TYPE	VISCOSITY (cP)	SETTING TIME (minutes)	SHEAR STRENGTH (gm/cm^2)
Bentonite	10-20	--	NA
Silicate	1.5-50	0.1-3000	1-150
Acrylamide	1.2-1.6	0.1-1000	20-200
Phenolic	1.2-10	1.5-2880	10-1200
Urethane	20-200	0.08-120	NA
Urea-Formaldehyde	10-13	1-60	NA
Epoxy	20-100	variable	NA
Polyester	10-200	15	NA

NA: Not available

Sources: Sommerer and Kitchens 1980
Tallard and Caron 1977a
Tallard and Caron 1977b
Karol 1982a
Bowen 1981
Avanti International 1982

Short term deterioration of the grout can be caused by rapid chemical degradation or by an incorrect setting time. The effect on setting time can be caused by a miscalculation of the grout formulation, dilution of the grout by groundwater, or changes caused by chemicals contained within the grouted strata. The effect that chemicals in the groundwater have on grout performance is addressed in Section 6, which provides information on the effect that different classes of chemicals will have on the set time and durability of each grout type.

The effect that groundwater will have on the stability of grout depends on the grout class and formulation. For areas that have large groundwater flow rates, the grout must be able to quickly set before it is diluted or washed away. The set time is, in many cases, a controlable parameter. Ranges of set times for the different classes of grouts are illustrated in Table 9. Water can also redissolve some of the grout constituents due to the reversibility of many of the polymerization or gellation reactions (Tallard and Caron 1977b).

The actual durability of a grout in a specific geological setting should be determined by laboratory testing. The selection of grout could also be based on the results of actual field applications in similar geologic settings.

OTHER FACTORS

Another grout selection factor that might be considered is the toxicity of the grout's components and the solidified grout. This factor will be important if the aquifer with which the grout comes in contact is a potential drinking water source. The oral toxicity of most of the compounds used in grouts has been determined as have many of the values for the set grout. Table 10 shows LD_{50} values for some of the commonly used grout materials. These values provide only an indication of the potential risk that a grout poses to the groundwater. The specific grout application and the amount of unreacted material must also be considered.

The cost of the grouting operation is also a factor that must be considered. This should include the costs of the materials as well as the injection costs. Current costs for grouted soils range from \$100/yd^3 to \$500/yd^3 of grouted soil, depending on the type of grout used and the characteristics of the soil. For chemical grouts, their expense is offset to some degree by the fact that particulate grouts may be three to five times more costly to pump into the ground (Guertin and McTigue 1982). Table 11 gives some costs of selected grouting materials.

OVERVIEW

By going through this process in a step-wise fashion, a number of candidate grouts can be selected. Unfortunately, there is not enough information available to create a series of tables listing all relevant selection factors. Much of this information must be collected for each specific site due to the wide variation of environmental and geological considerations.

TABLE 10. TOXICITY OF SELECTED GROUTS ORAL LD_{50} (mg/kg) FOR RATS

GROUT TYPE	COMPONENTS	ORAL LD_{50} (mg/kg) COMPONENTS	ORAL LD_{50} (mg/kg) SET GROUT
Silicate	-	-	>15,000
	Sodium Silicate	1100	-
	Calcium Chloride	1000	-
	Magnesium Chloride	2800	-
	Dimethylformamide	1500	-
Acrylamide	-	-	5,000
	Acrylamide Monomer	200	-
	Mechylenebiracrylamide	390	-
Phenolic	-	-	>15,000
	Resorcin	301	-
	Phenol	414	-
	Formaldehyde	800	-
Urethane	-	-	5,000
	Toluene Diisocyanate	5800	-
	Acetone	9750	-
Urea-Formaldehyde	-	-	NA
	Formaldehyde	800	-

Sources: Tallard and Caron 1977b
Berry 1982
Geochemical Corporation 1982

TABLE 11. APPROXIMATE COST OF GROUT[1]

GROUT TYPE	APPROXIMATE COST $/GALLON OF SOLUTION
Portland cement	0.95
Bentonite	1.25
Silicate - 20%	1.75
- 30%	2.10
- 40%	2.75
Lignochrome	1.55
Acrylamide	6.65
Urea-formaldehyde	5.70

[1] 1980 Dollars
Source: JRB Associates 1982

SECTION 9

RESEARCH NEEDS

During the course of this study several areas were identified that lacked available information but are important in determining the usefulness of grouts at hazardous waste disposal sites. These areas would be good candidates for further research and include:

- Grout specifications and applications
- Compatibility of grouts with chemicals
- Long-term stability of grout
- Compatibility testing procedures.

The specific topics that are included in these general areas are discussed in the following subsections.

GROUT SPECIFICATIONS AND APPLICATIONS

During the information search, very little data were found on the formulation of currently or potentially utilized grouts and their specific areas of application. Information on the chemical make-up and specific area of application of each type of grout must be known in order to select the grouts and testing procedures to be included in a laboratory evaluation program. The specific areas that should be investigated include:

- Areas of potential and actual grout application at waste disposal sites
- Information on actual grout formulations currently utilized.

COMPATIBILITY OF GROUTS WITH CHEMICALS

As noted in the text, there is very limited information on the effect chemicals would have on grouts utilized at disposal sites. Moreover, most compatibility information deals with the effects of high concentrations of simple chemicals. In order to evaluate the affect of leachates on grouts, information on compatibility of grouts with low chemical concentrations and chemical mixtures must be known. Thus, areas for further research including a pilot scale program are:

- Effects of dilute chemicals on grouts

- Effects of chemical mixtures on grouts
- Effects of actual leachates on grouts.

LONG-RANGE STABILITY OF GROUTS

Once in the ground, the ability of grout to withstand not only leachate but water, hydrostatic pressure, and biodegradation, must be known. This type of information is very limited in the literature and is very important if a permanent seal is to be obtained. Thus, the environmental effects on the structural integrity of grouts should be further researched in both a laboratory and pilot scale program.

COMPATIBILITY TESTING PROCEDURES

There currently are no established compatibility testing procedure for grouts. However, there is the potential to utilize the same types of testing procedures developed for evaluating soils, bentonite slurries, and cement. Permeability measurement techniques have been developed in all of these areas, which are directly applicable to grout compatibility evaluations. Set time measurements, on the other hand, are a little more difficult to apply because of the greatly varying nature of the set grouts. For both types of measurements, though, different laboratory techniques have to be used for testing the different grout types due to variation in physical/chemical properties. The areas that need further research include:

- Evaluation and selection of permeability testing procedures
- Evaluation and selection of set time testing procedures.

REFERENCES

ACI Committee 515. A Guide to the Use of Waterproofing, Dampproofing, Protective, and Decorative Barrier Systems for Concrete. ACI Report 515.IR-79. American Concrete Institute, Detroit, MI. 1979.

Alther, G. The Application of Bentonite as a Liner for Waste Containment. Section 1. General Classification of Wastes and Liners. International Minerals and Chemical Corporation, Des Plaines, IL. 1981a.

American Society for Testing and Materials (ASTM). 1982 Annual Book of ASTM Standards. Part 16. Chemical-Resistant Materials; Vitrified Clay, Concrete, Fiber--Cement Products; Mortars; Masonry. American Society for Testing and Materials, Philadelphia, PA 1982.

Anderson, D. and K.W. Brown. Organic Leachate Effects on the Permeability of Clay Liners. In: Land Disposal: Hazardous Waste. Proceedings of the Seventh Annual Research Symposium. EPA 600/9-81-002b. USEPA, Municipal Environmental Research Laboratory, Cincinnati, OH. 1981.

Anderson, D., K.W. Brown, and J. Green. Effect of Organic Fluids on the Permeability of Clay Soil Liners. In: Land Disposal of Hazardous Waste. Proceedings of the Eighth Annual Research Symposium. EPA 600/9-82-002. USEPA, Municipal Environmental Research Laboratory, Cincinnati, OH. 1982.

API. American Petroleum Institute. API Recommended Practice: Standard Procedure for Testing Drilling Fluids. API RP13B. American Petroleum Institute, Dallas, TX. 1982.

API. American Petroleum Institute. API Specification for Materials and Testing for Well Cements. API Spec. 10. American Petroleum Institute, Washington, DC. 1982.

Baker, W.H. Planning and Performing Structural Chemical Grouting. In: Proceedings of the Conference on Grouting in Geotechnical Engineering. American Society of Civil Engineers, NY. 1982.

Berry, R.M. Injectite-80 Polyacrylamide Grout. In: Proceedings of the Conference on Grouting in Geotechnical Engineering, American Society of Civil Engineers, NY 1982.

Billmeyer, F.W., Jr. Textbook of Polymer Science. 2nd ed. Wiley-Interscience, NY. 1971.

Boova, A.A. Furans as Chemical Construction Materials. In: Corrosion '77, The International Forum Devoted Exclusively to the Protection and Performance of Materials, March 14-18, San Francisco, CA. 1977.

Borden, R.H., R.J. Krizek, and W.H. Baker. Creep Behavior of Silicate Grouted Sand. In: Proceedings of the Conference on Grouting in Geotechnical Engineering, American Society of Civil Engineers, NY. 1981.

Bowen, R. Grouting in Engineering Practice. 2nd ed. John Wiley and Sons, NY. 1981.

Boyes, R.G.H. Structural and Cut-Off Diaphragm Walls. Applied Science Publishers Ltd., London, England. 1975.

Brady, N.C. The Nature and Properties of Soils. Macmillan Publishing Co., Inc., NY. 1974.

Caron, C. The Development of Grouts for the Injection of Fine Sands. In: Grouts and Drilling Muds in Engineering Practice. Butterworths, London. pp. 136-141. 1963.

Caron, C. The State of Grouting in the 1980's. In: Proceedings of the Conference on Grouting in Geotechnical Engineering, American Society of Civil Engineers, NY. 1982.

Case International Company. Case Slurry Wall Notebook Manufacturers Data. Case International Company, Houston, TX. 1982.

Chung, N.K. Investigation of Use of Gel Material for Mine Sealing. EPA-R2-72-135. Dravo Corporation. Prepared for: USEPA, Office of Research and Monitoring, Washington, DC. 1973.

Clarke, W.J. Performance Characteristics of Acrylate Polymer Grout. In: Proceedings of the Conference on Grouting in Geotechnical Engineering, American Society of Civil Engineers, NY. 1982.

Clough, G.W., D. Tan, W. Kuch and R. Koenyen. Development of Design Procedures for Stabilized Soil Support Systems for Soft Ground Tunneling - Volume II Preliminary Results. DOT-TST-77-74. U.S. Department of Transportation. Washington, DC. 1977.

Cotton, A.F. and G. Wilkinson. Advanced Inorganic Chemistry. 3rd ed. Interscience Publishers, New york, NY. 1972.

Cues, Inc. Q-Seal. Technical Product Information. 1982.

D'Appolonia, D.J. Slurry Trench Cut-Off Walls for Hazardous Waste Isolation. unpublished paper, Engineered Construction International, Inc., Pittsburgh, PA. April 1980a.

D'Appolonia, D.J. and C.R. Ryan. Soil-Bentonite Slurry Trench Cut-Off Walls. Engineered Construction International, Inc. Presented at Geotechnical Exhibition and Technical Conference, Chicago, IL. March 26, 1979.

Engineering News-Record. Epoxy Seals Leaking Salt Mine Shaft. p. 119. November 18, 1965.

Engineering News-Record. Seepage through dam checked by injecting Chrome-Lignin. Vol. 151, No. 15. p. 247. October 8, 1953.

Flatau, A.S., R.W. Brockett, and J.V. Brown. Grouts and Grouting. A Survey of Materials and Practice. Civil Engineering and Public Works Review. Vol. 68, No. 804. pp. 591-601. 1972.

Fung, R. (ed.) Protective Barriers for Containment of Toxic Materials. Noyes Data Corporation, Park Ridge, NJ. 1980.

Geochemical Corporation. Geo/Chem AC-400 Chemical Grout. Product Bulletin. 1982.

Greenwood, D.A. and J.F. Raffle. Formulation and Application of Grouts Containing Clay. In: Grouts and Drilling Muds in Engineering Practices. Butterworths, London. pp. 127-130. 1963.

Grim, R.E. and N. Guven. Bentonites. Geology Mineralogy. McGraw-Hill Book Company, New York, NY. 1978.

Guertin J.D. and W.H. McTigue. Volume 1. Groundwater Control Systems for Urban Tunneling. FHWA/RD-81/073. Goldberg, Zonio & Associates, Inc. Prepared for: U.S. Department of Transportation, Federal Highway Administration. Washington, DC. 1982.

Gutt, W.H. and W.H. Harrison. Chemical Resistance of Concrete. Concrete. pp. 35-37. May 1977.

Harr, M.E., S. Diamond, and F. Schmednecht. Vibrated-Beam Placed Thin Slurry Walls for Construction Dewatering, Water Conservation, Industrial Waste Ponding, and Other Applications. M.E. Harr Enterprises, Inc. (West Lafayette, IN); Sidney Diamond and Associates, Inc. (West Lafayette, IN); and Slurry Systems, Inc. (Gary, IN).

Hartley, J.N., P.L. Koehmstedt, D.J. Esterl, H.D. Freeman, J.L. Buelt, D.A. Nelson, and M.R. Elmore. Asphalt Emulsion Sealing of Uranium Mill Tailings. 1980 Annual Report. Pacific Northwest Laboratory. Prepared for: U.S. Department of Energy. May 1981.

Haxo, H.E., Jr. Interaction of Selected Lining Materials with Various Hazardous Wastes--II. In: Disposal of Hazardous Waste. Proceedings of the Sixth Annual Research Symposium. EPA 600/9-80-010. USEPA, Municipal Environmental Research Laboratory, Cincinnati, OH. 1980.

Haxo, H.E., Jr. Effects on Liner Materials of Long-Term Exposure in Waste Environments. In: Land Disposal of Hazardous Waste. Proceedings of the Eighth Annual Research Symposium. EPA 600/9-82-002. USEPA, Municipal Environmental Research Laboratory, Cincinnati, OH. 1982.

Hayward Baker Company, EarthTech Research Corporation, and ENSCO, Inc. Chemical Soil Grouting. Improved Design and Control. Draft. Federal Highway Administration, Fairbank Highway Research Station, McLean, VA. 1980.

Herndon, J. and T. Lenahan. Grouting in Soils. Volume 1. A State-of-the-Art Report. FHWA-RD-76-26. Halliburton Services. Prepared for: USDOT, Federal Highway Administration, Washington, DC. 1976a.

Herndon, J. and T. Lenahan. Grouting Soils. Volume 2. Design and Operation Manual. FHWA-RD-76-27. Halliburton Services. Prepared for: USDOT, Federal Highway Administration, Washington, DC. 1976b.

Huibregtse, K.R. and K.H. Kastman. Development of a System to Protect Groundwater Threatened by Hazardous Spills on Land. EPA 600/2-81-085. Rexnord, Inc. and Soil Testing Services, Inc. Prepared for: USEPA, Office of Research and Development, Industrial Environmental Research Laboratory, Edison, NJ. May 1981.

Hurley, C.H. and T.H. Thornburn. Sodium Silicate Stabilization of Soils - A Review of the Literature. UILU-ENG-71-2007. University of Illinois, Urbana, IL. 1971.

Ingles, O.G. and J.B. Metcalf. Soil Stabilization. Principles and Practice. John Wiley and Sons, NY. 1973.

Jaques, W.B. Stopping water with chemical grout. Civil Engineering. December 1981.

Jefferis, S.A. Bentonite--Cement Slurries for Hydraulic Cut-Offs. In: Proceedings of the Tenth International Conference on Soil Mechanics and Foundation Engineering, Volume 1, Stockholm, June 15-19, 1981. A.A. Balkema, Rotterdam. pp. 435-440. 1981.

Jiacai, L., Bacchang, W., Wengguang, C., Yuhua, G., and Hesheng, C. Polyurethane Grouting in Hydraulic Engineering.

Johnson, R. Grouting Silt and Sand at Low Temperatures. A Laboratory Investigation. CRREL Report 79-5. U.S. Army Cold Regions Research and Engineering Laboratory, Hanover, NH. March 1979.

JRB Associates. Handbook. Remedial Action at Waste Disposal Sites. EPA 625/6-82-006. USEPA, Municipal Environmental Research Laboratory, Cincinnati, OH. 1982.

Karol, R.H. Chemical Grouts and Their Properties. In: Proceedings of the Conference on Grouting in Geotechnical Engineering, American Society of Civil Engineers, NY. 1982a.

Karol, R.H. Seepage Control with Chemical Grout. In: Proceedings of the Conference on Grouting in Geotechnical Engineering, American Society of Civil Engineers, NY. 1982b.

Kirk-Othmer Encyclopedia of Chemical Technology. Vol. 5. 3rd ed. John Wiley & Sons, NY. 1979.

Kirk-Othmer Encyclopedia of Chemical Technology. Vol. 3. 3rd ed. john Wiley and Sons, New York, NY. 1978a.

Kirk-Othmer Encyclopedia of Chemical Technology. Vol. 2. 3rd ed. John Wiley and Sons, New York, NY. 1978b.

Koehmstedt, P.L., J.N. Hartley and D.K. Davis. Use of Asphalt Emulsion Sealants to Contain Radon and Radium in Uranium Tailings. BNWL-2190. Battelle Pacific Northwest Laboratories, Richland, WA. January 1977.

Lenahan, T. There is a Place For Grouting in Underground Storage Caverns. Bulletin of the Association of Engineering Geologists. Vol. X, No. 2. pp. 137-144. 1973.

Leonard, M.W. and J.A. Dempsey. Clays for Clay Grouting. In: Grouts and Drilling Muds in Engineering Practices. Butterworths, London. pp. 119-130. 1963.

Littlejohn, G.S. Design of Cement Based Grouts. In: Proceedings of the Conference on Grouting in Geotechnical Engineering, American Society of Civil Engineers, NY. 1982.

Malone, P.G., L.W. Jones, and R.J. Larson. Guide to the Disposal of Chemically Stabilized and Solidified Wastes. SW-872. U.S. Army Engineer Waterways Experiment Station. Prepared for: USEPA, Municipal Environmental Research Laboratory, Cincinnati, OH. 1980.

Matrecon, Inc. Lining of Waste Impoundment and Disposal Facilities. SW-870. USEPA, Municipal Environmental Research Laboratory, Cincinnati, OH. 1980.

McCabe, K.W. Polyurethane gives stabilty to mine roofs. Modern Plastics. January 1982.

Meyer, B. Urea-Formaldehyde Resins. Addison-Wesley. Publishing Company, Inc., London. 1979.

Millet, R.A. and J.Y. Perez. Current USA Practice: Slurry Wall Specifications. Journal of the Geotechnical Engineering Division. Vol. 107, No. 8. pp. 1041-1056. 1981.

Mobay Chemical Corporation. Roklok Binder. Technical Information. 1982.

Modern Plastics Encyclopedia. Vol. 58, No. 10A. McGraw-Hill, Inc., NY. 1981.

Morrison, R.T. amd R. N. Boyd. Organic Chemistry. 2nd ed. Allyn and Bacon, Inc., Boston, MA. 1969.

Neelands, R.J. and A.N. James. Formulation and Selection of Chemical Grouts with Typical Examples of their Field Use. In: Grouts and Drilling Muds in Engineering Practice. Butterworths, London. pp. 150-155. 1963.

Neville, A.M. Properties of Concrete. 2nd ed. John Wiley and Sons, New York, NY. 1973.

Office of the Chief of Engineers. Engineering Design. Chemical Grouting. EM 1110-2-3504. Department of the Army, Washington, DC. May 1973.

Office of the Chief of Engineers. Engineering and Design. Laboratory Soils Testing. EM 110-2-1906. Department of the Army, Washington, DC. 1970.

Olson, R.E. and D.E. Daniels. Measurement of the Hydraulic Conductivity of Fine-grained Soils, in Zimmie, T.T. and C.O. Riggs (eds.): Permeability of Groundwater Contaminant Transport, ASTM Special Technical Publication 746. American Society for Testing and Materials, Philadelphia, PA. pp. 18-64. 1981.

Perrott, W.E. British Practice for Grouting Soils. Journal of the Soil Mechanics and Foundations Division, Proceedings of the ASCE. Vol. 91, No. SM 6. pp. 57-79. 1965.

Rensvold, R.F. Epoxy Resin Grouting Fluid and Method for Stabilizing Earth Formations. (To Halliburton Co.) U.S. Patent No. 3,416,604. December 17, 1968.

Rogoshewski, P., H. Bryson, P. Lee, K. Wagner, P. Spooner, and S. Paige. Manual for Remedial Actions at Waste Disposal Sites. JRB Associates. Prepared for: USEPA, Region II, Office of Research and Development, New York, NY. 1980.

Saunders, J.H. and K.C. Frisch. Polyurethanes. Chemistry and Technology. part I. Chemistry. Wiley-Interscience Publishers, NY. 1962.

Scheldknecht, C.E. and Skeist, I. (eds.) Polymerization Processes. Wiley-Interscience Publishers, New York, NY. 1977.

Scott, R.L. and R.M. Hays. Inactive and Abandoned Underground Mines--Water Pollution Prevention and Control. EPA 440/9-75-007. Michael Baker, Jr., Inc. Prepared for: USEPA, Office of Water Planning and Standards, Washington, DC. 1975.

Shuckrow A.J., A.P. Pajak, and C.J. Touhill. Management of Hazardous Waste Leachate. U.S. Environmental Protection Agency Municipal Environmental Research Laboratory, Cincinnati, OH 1980.

Slurry Systems. General Information on ASPEMIX Slurry Test on Various Leachates. Slurry Systems, Gary, IN. March 25, 1982.

Soletanche. Consolidation of Fissured Rocks by High Pressure Grouting. gyf-pc.mm No. 10.271. Paris. 1962.

Sommerer, S. and J.F. Kitchens. Engineering and Development Support of General Decon Technology for the DARCOM Installation Restoration Program. Task 1 Literature Review on Groundwater Containment and Diversion Barriers. Draft. Atlantic Research Corporation. Prepared for: U.S. Army Hazardous Materials Agency, Aberdeen Proving Ground, MD. October 1980.

Spangler, M.G. and R.L. Handy. Soil Engineering. In Text. Harper and Rowe Publishers, New York. 1973.

Tallard, G.R. and C. Caron. Chemical Grouts for Soils. Vol. I Available Materials. FHWA-RD-77-50. Soletanche and Rodio, Inc. Prepared for: United States Department of Transportation, Federal Highway Administration, Offices of Research and Development, Washington, DC. June 1977a.

Tallard, G.R and C. Caron. Chemical Grouts for Soils. Vol. II Engineering Evaluation of Available Materials. FHWA - RD-77-51. Soletache and Rodeo, Inc. Prepared for: United States Department of Transportation, Federal Highway Administration, Offices of Research and Development, Washingon, D.C. June 1977b.

Thompson, D.W., P.G. Malone, and L.W. Jones. Survey of Available Stabilization Technology. In: Toxic and Hazardous Waste Disposal. Volume I. Processes for Stabilization/Solidification. Ann Arbor Science Publishers, Inc., Ann Arbor, MI. 1980.

Tiedemann, H.R. and J. Graver. Groundwater Control in Tunneling. Vol. 2--Preventing Groundwater Intrusion into Completed Transportation Tunnels. FHWA/RD-81/074. Jacobs Associates. Prepared for: USDOT, Federal Highway Administration, Washington, DC. 1982.

Tomlinson, M.J. Foundation Design and Construction. 4th ed. Pitman Advanced Publishing Program, Boston, MA. 1980.

U.S. Grout Corporation. Grouting Handbook. A Professional's Guide to Non-Shrink Grouting for: Owners, Architects, Engineers, Contractors, and Specifiers. Fairfield, CT. 1981.

Vinson, T.S. and J.K. Mitchell. Poly-urethane Foamed Plastics in Soil Grouting. Journal of the Soil Mechanics and Foundations Division. Proceedings of the ASCE. Vol. 98, No. SM 6, pp. 579-602. 1972.

Weast, R.C. (ed.) Handbook of Chemistry and Physics. 52nd ed. CRC Press. Cleveland, OH. 1972.

Xanthakos, P.P. Slurry Walls. McGraw-Hill Book Company, New York. 1979.

Zimmie, T.F. Geotechnical Testing Considerations in the Determination of Laboratory Permeability for Hazardous Waste Disposal Siting. In Conway, R.C. and B.C. Malloy (eds.): Hazardous Solid Waste Testing, ASTM Special Technical Publication 760. American Society for Testing and Materials, Philadelphia, PA. pp. 209-304. 1981.

BIBLIOGRAPHY

ACI Committee 515. A Guide to the Use of Waterproofing, Dampproofing, Protective, and Decorative Barrier Systems for Concrete. ACI Report 515.IR-79. American Concrete Institute, Detroit, MI. 1979.

Alther, G. The Application of Bentonite as a Liner for Waste Containment. Section 1. General Classification of Wastes and Liners. International Minerals and Chemical Corporation, Des Plaines, IL. 1981a.

Alther, G.R. The Role of Bentonite in Soil Sealing Applications. International Sealing Applications. International Minerals and Chemical Corporation, Des Plaines, IL 1981b.

Ambraseys, N.N. Cut-Off Efficiency of Grout Curtains and Slurry Trenches. In: Grouts and Drilling Muds in Engineering Practice. Butterworths, London. pp. 43-46. 1963.

American Society for Testing and Materials (ASTM). 1982 Annual Book of ASTM Standards. P[illegible]16. Chemical-Resistant Materials; Vitrified Clay, Concrete, F[illegible]-Cement Products; Mortars; Masonry. American Society for Testing and Materials, Philadelphia, PA 1982.

Anderson, D. and K.W. Brown. Organic Leachate Effects on the Permeability of Clay Liners. In: Land Disposal: Hazardous Waste. Proceedings of the Seventh Annual Research Symposium. EPA 600/9-81-002b. USEPA, Municipal Environmental Research Laboratory, Cincinnati, OH. 1981.

Anderson, D., K.W. Brown, and J. Green. Effect of Organic Fluids on the Permeability of Clay Soil Liners. In: Land Disposal of Hazardous Waste. Proceedings of the Eighth Annual Research Symposium. EPA 600/9-82-002. USEPA, Municipal Environmental Research Laboratory, Cincinnati, OH. 1982.

Ando, S. and M. Makita. Environmental Impacts on Groundwater by Chemical Grouting. In: Proceedings of the Specialty Session on Geotechnical Engineering and Environmental Control. Ninth International Conference on Soil Mechanics and Foundation Engineering. Tokyo, Japan. July 1977.

API. American Petroleum Institute. API Recommended Practice: Standard Procedure for Testing Drilling Fluids. API RP13B. American Petroleum Institute, Dallas, TX. 1982.

API. American Petroleum Institute. API Specification for Materials and Testing for Well Cements. API Spec. 10. American Petroleum Institute, Washington, DC. 1982.

Avanti International. Grouting Manual. Avanti International, Houston, TX. 1982.

Avanti International. AV-100 Chemical Grout. Safe Operating Practices Program. Houston, TX. 1978-1979.

Baker, W.H. Planning and Performing Structural Chemical Grouting. In: Proceedings of the Conference on Grouting in Geotechnical Engineering. American Society of Civil Engineers, NY. 1982

Berry, R.M. Injectite-80 Polyacrylamide Grout. In: Proceedings of the Conference on Grouting in Geotechnical Engineering, American Society of Civil Engineers, NY 1982

Billmeyer, F.W., Jr. Textbook of Polymer Science. 2nd ed. Wiley-Interscience, NY. 1971.

Boova, A.A. Furans as Chemical Construction Materials. In: Corrosion '77, The International Forum Devoted Exclusively to the Protection and Performance of Materials, March 14-18, San Francisco, CA. 1977.

Borden, R.H., R.J. Krizek, and W.H. Baker. Creep Behavior of Silicate Grouted Sand. In: Proceedings of the Conference on Grouting in Geotechnical Engineering, American Society of Civil Engineers, NY. 1981.

Bowen, R. Grouting in Engineering Practice. 2nd ed. John Wiley and Sons, NY. 1981.

Boyes, R.G.H. Structural and Cut-Off Diaphragm Walls. Applied Science Publishers Ltd., London, England. 1975

Brady, N.C. The Nature and Properties of Soils. Macmillan Publishing Co., Inc., NY. 1974.

Brown, K.W. and D. Anderson. Effect of Organic Chemicals on Clay Liner Permeability. A Review of the Literature. In: Disposal of Hazardous Waste. Proceedings of the Sixth Annual Research Symposium. EPA 600/9-80-010. USEPA, Municipal Environmental Research Laboratory. Cincinnati, OH. 1980.

Bussey, W.H. Some Rock-grouting Experiences. In: Grouts and Drilling Muds in Engineering Practice. Butterworths, London. pp. 65-69. 1963.

Bussey, W.H. Suspension Grouts and Their Injection. *Bulletin of the Association of Engineering Geologists*. Vol. X, No. 4. pp. 313-323. 1973.

Calhoun, T.P. Longevity of Sewer Grout Under Severe Conditions. Public Works. Vol. 106, No. 10. p. 80. 1975.

Caron, C. The Development of Grouts for the Injection of Fine Sands. In: Grouts and Drilling Muds in Engineering Practice. Butterworths, London. pp. 136-141. 1963.

Caron, C. The State of Grouting in the 1980's. In: Proceedings of the Conference on Grouting in Geotechnical Engineering, American Society of Civil Engineers, NY. 1982.

Case International Company. Case Slurry Wall Notebook Manufacturers Data. Case International Company, Houston, TX. 1982.

Chemical Processing. Specially processed bentonite seals ponds against seepage. pp. 40-41. September 1979.

Chung, N.K. Investigation of Use of Gel Material for Mine Sealing. EPA-R2-72-135. Dravo Corporation. Prepared for: USEPA, Office of Research and Monitoring, Washington, DC. 1973.

Clarke, W.J. Performance Characteristics of Acrylate Polymer Grout. In: Proceedings of the Conference on Grouting in Geotechnical Engineering, American Society of Civil Engineers, NY. 1982.

Clough, G.W., D. Tan, W. Kuch and R. Koenyen. Development of Design Procedures for Stabilized Soil Support Systems for Soft Ground Tunneling - Volume II Preliminary Results. DOT-TST-77-74. U.S. Department of Transportation. Washington, DC. 1977.

Committee on Grouting. Preliminary Glossary of Terms Relating to Grouting. Journal of the Geotechnical Engineering Division, Proceedings of the ASCE. Vol. 106, GT7. pp. 803-815. 1980.

Committee on Grouting. Guide Specifications for Chemical Grouts. Journal of the Soil Mechanics and Foundations Division Proceedings of the ASCE. pp. 346-352. March 1968.

Cotton, A.F. and G. Wilkinson. Advanced Inorganic Chemistry. 3rd ed. Interscience Publishers, New york, NY. 1972.

Cues, Inc. Q-Seal. Technical Product Information. 1982.

D'Appolonia, D.J. Slurry Trench Cut-Off Walls for Hazardous Waste Isolation. Engineered Construction International, Inc., Pittsburgh, PA. April 1980a.

D'Appolonia, D.J. Soil-Bentonite Slurry Trench Cut-Offs. Journal of the Geotechnical Engineering Division, ASCE. No. GT4. pp. 399-417. April 1980b.

D'Appolonia, D.J. and C.R. Ryan. Soil-Bentonite Slurry Trench Cut-Off Walls. Engineered Construction International, Inc. Presented at Geotechnical Exhibition and Technical Conference, Chicago, IL. March 26, 1979.

Dragun, J. and C.S. Helling. Soil- and Clay-Catalyzed Reactions: I. Physico-chemical and Structural Relationships of Organic Chemicals Undergoing Free-Radical Oxidation. In: Land Disposal of Hazardous Waste. Proceedings of the Eighth Annual Research Symposium. EPA-600/9-82-002. USEPA, Municipal Environmental Laboratory, Cincinnati, OH. March 1982.

Engineering News-Record. Epoxy Seals Leaking Salt Mine Shaft. p. 119. November 18, 1965.

Engineering News-Record. Seepage through dam checked by injecting Chrome-Lignin. Vol. 151, No. 15. p. 247. October 8, 1953.

Farkas, L.W. and M.M Szwere. Acid Resisting Cement and Method of Making. U.S. Patent No. 2,492,790. December 27, 1949.

Fern, K.A. The Application of Polymerization Techniques to the Solution of Grouting Problems. In: Grouts and Drilling Muds in Engineering Practice. Butterworths, London. pp. 146-149. 1963.

Flatau, A.S., R.W. Brockett, and J.V. Brown. Grouts and Grouting. A Survey of Materials and Practice. Civil Engineering and Public Works Review. Vol. 68, No. 804. pp. 591-601. 1972.

French Association of Underground Construction. Recommendations for the Use of Grouting in Underground Construction. 1975.

Fuller, W.H. Project Summary. Liners of Natural Porous Materials to Minimize Pollutant Migration. EPA-600/S2-81-122. USEPA, Municipal Environmental Research Laboratory. Cincinnati, OH. July 1981.

Fung, R. (ed.) Protective Barriers for Containment of Toxic Materials. Noyes Data Corporation, Park Ridge, NJ. 1980.

Furr, H.L. and L.L. Ingram. Bond and Durability of Concrete and Resinous Overlays. Research Report 130-5. Study 2-18-68-130. Texas Transportation Institute and Texas Highway Department. 1971.

Geochemical Corporation. Geo/Chem AC-400 Chemical Grout. Product Bulletin. 1982.

Greenwood, D.A. and J.F. Raffle. Formulation and Application of Grouts Containing Clay. In: Grouts and Drilling Muds in Engineering Practices. Butterworths, London. pp. 127-130. 1963.

Griffin, R.A., K. Cartwright, N.F. Shimp, J.D. Steele, R.R. Ruch, W.A. White, G.M. Hughes, and R.H. Gilkeson. Attenuation of Pollutants in Municipal Landfill Leachate by Clay Minerals. Part 1 - Column Leaching and Field Verification. Environmental Geology Notes 78. Illinois Geological Survey. Urbana, IL. 1976.

Griffin, R.A. and N.F. Shimp. Attenuation of Pollutants in Municipal Landfill Leachate by Clay Minerals. EPA 600/2-78-157. Illinois State Geological Survey. Prepared by: USEPA, Municipal Environmental Research Laboratory. Cinncinnati, OH. 1978.

Grim, R.E. and N. Guven. Bentonites. Geology Mineralogy. McGraw-Hill Book Company, New York, NY. 1978.

Grouts and Drilling Muds in Engineering Practice. Discussion (Papers 1 to 7). Butterworths, London. pp. 47-62. 1963a.

Grouts and Drilling Muds in Engineering Practice. Discussion (Papers 15 to 22). Butterworths, London. pp. 164-174. 1963a.

Guertin J.D. and W.H. McTigue. Volume 1. Groundwater Control Systems for Urban Tunneling. FHWA/RD-81/073. Goldberg, Zonio & Associates, Inc. Prepared for: U.S. Department of Transportation, Federal Highway Administration. Washington, DC. 1982.

Gutt, W.H. and W.H. Harrison. Chemical Resistance of Concrete. Concrete. pp. 35-37. May 1977.

Haffen, M. and J. Janin. Grouting of Cohesionless Water-Bearing Soils in City Tunnels. Soletanche and Rodio, Inc. Presented at: North American Rapid Excavation and Tunneling Conference, Chicago, IL. 1972.

Halliburton Company. Feasibility Study on the Application of Various Grouting Agents, Techniques and Methods to the Abatement of Mine Drainage Pollution. Part IV. Additional Laboratory and Field Tests for Evaluating and Improving Methods for Abating Mine Drainage Pollution. U.S. Department of the Interior, Federal Water Pollution Control Administration. 1968.

Harr, M.E., S. Diamond, and F. Schmednecht. Vibrated-Beam Placed Thin Slurry Walls for Construction Dewatering, Water Conservation, Industrial Waste Ponding, and Other Applications. M.E. Harr Enterprises, Inc. (West Lafayette, IN); Sidney Diamond and Associates, Inc. (West Lafayette, IN); and Slurry Systems, Inc. (Gary, IN).

Hartley, J.N., P.L. Koehmstedt, D.J. Esterl, H.D. Freeman, J.L. Buelt, D.A. Nelson, and M.R. Elmore. Asphalt Emulsion Sealing of Uranium Mill Tailings. 1980 Annual Report. Battelle Pacific Northwest Laboratory, Richland, Washington. Prepared for: U.S. Department of Energy. May 1981.

Hatayama, H.K., R.D. Stephens, E.R. de Vera, J.J. Chan, D.L. Storm. Hazardous Waste Compatibility. In: Disposal of Hazardous Waste. Proceedings of the Sixth Annual Research Symposium, Chicago, IL, March 17-20, 1980. EPA-600/9-80-010. USEPA, Municipal Environmental Laboratory, Cincinnati, OH. March 1980.

Haxo, H.E., Jr. Interaction of Selected Lining Materials with Various Hazardous Wastes--II. In: Disposal of Hazardous Waste. Proceedings of the Sixth Annual Research Symposium. EPA 600/9-80-010. USEPA, Municipal Environmental Research Laboratory, Cincinnati, OH. 1980.

Haxo, H.E., Jr. Durability of Liner Materials for Hazardous Waste Disposal Facilities. In: Land Disposal: Hazardous Waste. Proceedings of the Seventh Annual Research Symposium. EPA 600/9-81-002b. USEPA, Municipal Environmental Research Laboratory, Cincinnati, OH. 1981.

Haxo, H.E., Jr. Effects on Liner Materials of Long-Term Exposure in Waste Environments. In: Land Disposal of Hazardous Waste. Proceedings of the Eighth Annual Research Symposium. EPA 600/9-82-002. USEPA, Municipal Environmental Research Laboratory, Cincinnati, OH. 1982.

Haxo, H.E., Jr., R.S. Haxo, and R.M. White. Liner Materials Exposed to Hazardous and Toxic Sludges. First Interim Report. EPA 600/2-77-081. MATRECON, INC. Prepared for: USEPA, Municipal Environmental Research Laboratory, Cincinnati, OH. 1977.

Hayward Baker Company, EarthTech Research Corporation, and ENSCO, Inc. Chemical Soil Grouting. Improved Design and Control. Draft. Federal Highway Administration, Fairbank Highway Research Station, McLean, VA. 1980.

Herndon, J. and T. Lenahan. Grouting in Soils. Volume 1. A State-of-the-Art Report. FHWA-RD-76-26. Halliburton Services. Prepared for: USDOT, Federal Highway Administration, Washington, DC. 1976a.

Herndon, J. and T. Lenahan. Grouting Soils. Volume 2. Design and Operation Manual. FHWA-RD-76-27. Halliburton Services. Prepared for: USDOT, Federal Highway Administration, Washington, DC. 1976b.

Hilton, I.C. Grout Selection: A New Classification System. Civil Engineering and Public Works Review. pp. 993-995. September 1967.

Hoff, G.C. Investigation of Expanding Grout and Concrete. Report 1. Summary of Field Mixture Test Results, July 1969 through June 1970. Miscellaneous Paper C-71-5. U.S. Army Engineer Waterways Experiment Station, Vicksburg, MS. 1971.

Hoshiya, M., S. Shimade, H. Kanematu, and K. Kayahara. A New Grouting Material of Non-alkaline Silica Sol. In: Proceedings of the Conference on Grouting in Geotechnical Engineering, American Society of Civil Engineers, NY. 1982.

Huibregtse, K.R. and K.H. Kastman. Development of a System to Protect Groundwater Threatened by Hazardous Spills on Land. EPA 600/2-81-085. Rexnord, Inc. and Soil Testing Services, Inc. Prepared for: USEPA, Office of Research and Development, Industrial Environmental Research Laboratory, Edison, NJ. May 1981.

Huibregtse, K.R. and K.H. Kastman. Guide to Use of In-Situ Containment/Treatment Equipment. Rexnord, Inc. and Soil Testing Services, Inc. Prepared for: USEPA, Office of Research and Development, Industrial Environmental Research Laboratory, Edison, NJ.

Hurley, C.H. and T.H. Thornburn. Sodium Silicate Stabilization of Soils - A Review of the Literature. UILU-ENG-71-2007. University of Illinois, Urbana, IL. 1971.

Ingles, O.G. and J.B. Metcalf. Soil Stabilization. Principles and Practice. John Wiley and Sons, NY. 1973.

Injections. (Technical Bulletin.) Soletanche, Paris.

Janin, J.J. and G.F. Le Sciellour. Chemical Grouting for Paris Rapid Transit Tunnels. Journal of the Construction Division. Proceedings of the American Society of Civil Engineers. pp. 61-74. June 1970.

Jaques, W.B. Stopping water with chemical grout. Civil Engineering. December 1981.

Jefferis, S.A. Bentonite--Cement Slurries for Hydraulic Cut-Offs. In: Proceedings of the Tenth International Conference on Soil Mechanics and Foundation Engineering, Volume 1, Stockholm, June 15-19, 1981. A.A. Balkema, Rotterdam. pp. 435-440. 1981.

Jiacai, L., Bacchang, W., Wengguang, C., Yuhua, G., and Hesheng, C. Polyurethane Grouting in Hydraulic Engineering.

Johnson, R. Grouting Silt and Sand at Low Temperatures. A Laboratory Investigation. CRREL Report 79-5. U.S. Army Cold Regions Research and Engineering Laboratory, Hanover, NH. March 1979.

JRB Associates. Handbook. Remedial Action at Waste Disposal Sites. EPA 625/6-82-006. USEPA, Municipal Environmental Research Laboratory, Cincinnati, OH. 1982.

Karol, R.H. Chemical Grouts and Their Properties. In: Proceedings of the Conference on Grouting in Geotechnical Engineering, American Society of Civil Engineers, NY. 1982a.

Karol, R.H. Seepage Control with Chemical Grout. In: Proceedings of the Conference on Grouting in Geotechnical Engineering, American Society of Civil Engineers, NY. 1982b.

Karol, R.H. Chemical Grouting Technology. *Journal of the Soil Mechanics and Foundations Division*, Proceedings of the ASCE. Vol. 94, No. SM1. pp. 175-204. 1968.

Katti, R.K. and K.R. Kulkarni. A Study of Effect of Trace Inorganic Chemicals on Lime Stabilization of an Expansive Soil Sample from Poona. *Journal Indian Roads Congress*. Vol. 27. pp. 218-230. 1962.

Kingsbury, R.P. Position Paper. Chemical Resistance of Clays. American Colloid Company. 1982.

Kirk-Othmer Encyclopedia of Chemical Technology. Vol. 5. 3rd ed. John Wiley & Sons, NY. 1979.

Kirk-Othmer Encyclopedia of Chemical Technology. Vol. 3. 3rd ed. john Wiley and Sons, New York, NY. 1978a.

Kirk-Othmer Encyclopedia of Chemical Technology. Vol. 2. 3rd ed. John Wiley and Sons, New York, NY. 1978b.

Koch, R.R., J. Ramos, and H.C. McLaughlin. Composition and Method for Stabilization of Soil. (To Halliburton Co.) U.S. Patent No. 3,223,163. December 14, 1965.

Koehmstedt, P.L., J.N. Hartley and D.K. Davis. Use of Asphalt Emulsion Sealants to Contain Radon and Radium in Uranium Tailings. BNWL-2190. Battelle Pacific Northwest Laboratories, Richland, WA. January 1977.

Kurt, C.E. and R.C. Johnson, Jr. Permeability of Grout Seals Surrounding Thermoplastic Well Casing. *Groundwater*. Vol. 20, No. 4. pp. 415-419. 1982.

Lancaster-Jones, P.F.F. The interpretation of the Lugeon water-test. *Quarterly Journal of Engineering Geology*. Vol. 8, No. 2. pp. 151-154. 1975.

Lenahan, T. There is a Place For Grouting in Underground Storage Caverns. *Bulletin of the Association of Engineering Geologists*. Vol. X, No. 2. pp. 137-144. 1973.

Leonard, M.W. and J.A. Dempsey. Clays for Clay Grouting. In: Grouts and Drilling Muds in Engineering Practices. Butterworths, London. pp. 119-130. 1963.

Littlejohn, G.S. Design of Cement Based Grouts. In: Proceedings of the Conference on Grouting in Geotechnical Engineering, American Society of Civil Engineers, NY. 1982.

Lundberg, L.A., J.C. Schlegel, and J.E. Carpenter. Resinous Composition. (To American Cyanamid Co.) U.S. Patent No. 3,091,936. June 4, 1963.

Malone, P.G., L.W. Jones, and R.J. Larson. Guide to the Disposal of Chemically Stabilized and Solidified Wastes. SW-872. U.S. Army Engineer Waterways Experiment Station. Prepared for: USEPA, Municipal Environmental Research Laboratory, Cincinnati, OH. 1980.

Matrecon, Inc. Lining of Waste Impoundment and Disposal Facilities. SW-870. USEPA, Municipal Environmental Research Laboratory, Cincinnati, OH. 1980.

McCabe, K.W. Polyurethane gives stabilty to mine roofs. Modern Plastics. January 1982.

McLaughlin, H.C. Method of Stabilizing or Sealing Earth Formations. (To Halliburton Co.) U.S. Patent No. 3,334,689. August 8, 1967.

McLaughlin, H.C. Preparation and Use of Sodium Silicate Gels. (To Halliburton Co.) U.S. Patent No. 3,202,214. August 24, 1965.

Meyer, B. Urea-Formaldehyde Resins. Addison-Wesley. Publishing Company, Inc., London. 1979.

Miles, M.M. amd R.G.H. Boyes. Slurry trenching developments. Civil Engineering. pp. 51-52. April 1982.

Millet, R.A. and J.Y. Perez. Current USA Practice: Slurry Wall Specifications. Journal of the Geotechnical Engineering Division. Vol. 107, No. 8. pp. 1041-1056. 1981.

Mobay Chemical Corporation. Roklok Binder. Technical Information. 1982.

Modern Plastics Encyclopedia. Vol. 58, No. 10A. McGraw-Hill, Inc., NY. 1981.

Moller, K. Control of groundwater and unstable soils. Water Services. Vol. 80, No. 969. pp. 684-686. 1976.

Morrison, R.T. amd R. N. Boyd. Organic Chemistry. 2nd ed. Allyn and Bacon, Inc., Boston, MA. 1969.

Nasiatka, D.M., T.A. Shepherd, and J.D. Nelson. Clay Liner Permeability in Low pH Environments. In: Symposium on Uranium Mill Tailings Management, Fort Collins, CO. October 26-27, 1981.

Neelands, R.J. and A.N. James. Formulation and Selection of Chemical Grouts with Typical Examples of their Field Use. In: Grouts and Drilling Muds in Engineering Practice. Butterworths, London. pp. 150-155. 1963.

Neville, A.M. Properties of Concrete. 2nd ed. John Wiley and Sons, New York, NY. 1973.

Office of the Chief of Engineers. Engineering Design. Chemical Grouting. EM 1110-2-3504. Department of the Army, Washington, DC. May 1973.

Office of the Chief of Engineers. Engineering and Design. Laboratory Soils Testing. EM 110-2-1906. Department of the Army, Washington, DC. 1970.

Olson, R.E. and D.E. Daniels. Measurement of the Hydraulic Conductivity of Fine-grained Soils, in Zimmie, T.T. and C.O. Riggs (eds.): Permeability of Groundwater Contaminant Transport, ASTM Special Technical Publication 746. American Society for Testing and Materials, Philadelphia, PA. pp. 18-64. 1981.

Peeler, C.E. Chemical Composition and Process for Soil Stabilization. (To Diamond Alkali Co.) U.S. Patent No. 2,968,572. January 17, 1961.

Perrott, W.E. British Practice for Grouting Soils. *Journal of the Soil Mechanics and Foundations Division, Proceedings of the ASCE*. Vol. 91, No. SM 6. pp. 57-79. 1965.

Pusch, R. Rock Sealing with Bentonite by Means of Electrophoresis. *Bulletin of the International Association of Engineering Geology*. No. 18. pp. 187-190. 1978.

Rensvold, R.F. Epoxy Resin Grouting Fluid and Method for Stabilizing Earth Formations. (To Halliburton Co.) U.S. Patent No. 3,416,604. December 17, 1968.

Rhoderick, J.E. and A.D. Buck. Borehole Plugging Program (Waste Disposal). Report 2. Petrographic Examination of Several Four-Year Old Laboratory Developed Grout Mixtures. Miscellaneous Paper of C-78-1. U.S. Army Waterways Experiment Station, Vicksburg, MS. 1981.

Riedel, C.M. Chemical Soil Solidification--Theory and Applications in Construction Work. *Transaction of the New York Academy of Sciences*. Ser. II, Vol. 27, No. 2. pp. 189-202. 1964.

Rogoshewski, P., H. Bryson, P. Lee, K. Wagner, P. Spooner, and S. Paige. Manual for Remedial Actions at Waste Disposal Sites. JRB Associates. Prepared for: USEPA, Region II, Office of Research and Development, New York, NY. 1980.

Rollinger, G. Operations and Maintenance Manual. In-Situ Containment/ Treatment Equipment. Rexnord, Inc. Prepared for: USEPA, Office of Research and Development, Industrial Environmental Research Laboratory, Edison, NJ.

Rushing, H.B. Evaluation of Masonry Coatings. Research Project No. 68-3C(B). Louisiana Department of Highways, Materials Division. 1969.

Saunders, J.H. and K.C. Frisch. Polyurethanes. Chemistry and Technology. part I. Chemistry. Wiley-Interscience Publishers, NY. 1962.

Scheldknecht, C.E. and Skeist, I. (eds.) Polymerization Processes. Wiley-Interscience Publishers, New York, NY. 1977.

Schupack, F. Grouting of post-tensioning tendons. Civil Engineering. pp. 72-73. March 1978.

Scott, R.L. and R.M. Hays. Inactive and Abandoned Underground Mines--Water Pollution Prevention and Control. EPA 440/9-75-007. Michael Baker, Jr., Inc. Prepared for: USEPA, Office of Water Planning and Standards, Washington, DC. 1975.

Slurry Systems. General Information on ASPEMIX Slurry Test on Various Leachates. Slurry Systems, Gary, IN. March 25, 1982.

Soletanche. Soils Grouting. Technical Bulletin. Paris. No Date.

Soletanche. Consolidation of Fissured Rocks by High Pressure Grouting. gyf-pc.mm No. 10.271. Paris. 1962.

Sommerer, S. and J.F. Kitchens. Engineering and Development Support of General Decon Technology for the DARCOM Installation Restoration Program. Task 1 Literature Review on Groundwater Containment and Diversion Barriers. Draft. Atlantic Research Corporation. Prepared for: U.S. Army Hazardous Materials Agency, Aberdeen Proving Ground, MD. October 1980.

Spangler, M.G. and R.L. Handy. Soil Engineering. In Text. Harper and Rowe Publishers, New York. 1973.

Stewart, W.S. State-of-the-Art Study of Land Impoundment Techniques. EPA 600/2-78-196. Exxon Research and Engineering Company. Prepared for: USEPA, Municipal Environmental Research Laboratory, Cincinnati, OH. 1978.

Tallard, G.R. and C. Caron. Chemical Grouts for Soils. Vol. I Available Materials. FHWA-RD-77-50. Soletanche and Rodio, Inc. Prepared for: United States Department of Transportation, Federal Highway Administration, Offices of Research and Development, Washington, DC. June 1977a.

Tallard, G.R. and C. Caron. Chemical Grouts for Soils. Vol. II Engineering Evaluation of Available Materials. FHWA-RD-77-51. Soletanche and Rodio, Inc. Prepared for: United States Department of Transportation, Federal Highway Administration, Offices of Research and Development, Washington, DC. June 1977b.

Technical Information Center and Concrete Laboratory. Miscellaneous Paper C-78-8. Bibliography on Grouting. U.S. Army Engineer Waterways Experiment Station, Vicksburg, MS. June 1978.

Thompson, D.W., P.G. Malone, and L.W. Jones. Survey of Available Stabilization Technology. In: Toxic and Hazardous Waste Disposal. Volume I. Processes for Stabilization/Solidification. Ann Arbor Science Publishers, Inc., Ann Arbor, MI. 1980.

Urethane Grouts. Technical Information. 3M, St. Paul, MN. 1981-1982.

Sealing Gel System Field Manual. 3M, St. Paul, MN. August 1980.

Tiedemann, H.R. and J. Graver. Groundwater Control in Tunneling. Vol. 2--Preventing Groundwater Intrusion into Completed Transportation Tunnels. FHWA/RD-81/074. Jacobs Associates. Prepared for: USDOT, Federal Highway Administration, Washington, DC. 1982.

Tolman, A.L., A.P. Ballestero, Jr., W.W. Beck, Jr., and G.H. Emrich. Guidance Manual for Minimizing Pollution from Waste Disposal Sites. EPA 600/2-78-142. A.W. Martin Associates, Inc. Prepared for: USEPA, Municipal Environmental Research Laboratory, Cincinnati, OH. 1978

Tomlinson, M.J. Foundation Design and Construction. 4th ed. Pitman Advanced Publishing Program, Boston, MA. 1980.

U.S. Grout Corporation. Five Star Grout Technical Bulletins. Riverside, CT. 1980.

U.S. Grout Corporation. Grouting Handbook. A Professional's Guide to Non-Shrink Grouting for: Owners, Architects, Engineers, Contractors, and Specifiers. Fairfield, CT. 1981.

Vinson, T.S. and J.K. Mitchell. Poly-urethane Foamed Plastics in Soil Grouting. Journal of the Soil Mechanics and Foundations Division. Proceedings of the ASCE. Vol. 98, No. SM 6, pp. 579-602. 1972.

Walley, D.M. Investigation of the Resistance of Freshly Injected Grout to Erosion and Dilution by Flowing Water. Miscellaneous Paper C-76-4. U.S. Army Engineer Waterways Experiment Station, Vicksburg, MS. 1976.

Warner, J. Epoxies--"Miracle" materials don't always give miracle results. Civil Engineering. pp. 48-55. February 1978.

Watertight diaphragm walls. (Technical Bulletin.) Soletanche, Paris.

Weast, R.C. (ed.) Handbook of Chemistry and Physics. 52nd ed. CRC Press. Cleveland, OH. 1972.

Williams, D.R. Silicate Grout. (To The Cementation Co., Ltd., London.) U.S. Patent No. 3,294,563. December 27, 1966.

Xanthakos, P.P. Slurry Walls. McGraw-Hill Book Company, New York. 1979.

Zimmie, T.F. Geotechnical Testing Considerations in the Determination of Laboratory Permeability for Hazardous Waste Disposal Siting. In Conway, R.C. and B.C. Malloy (eds.): Hazardous Solid Waste Testing, ASTM Special Technical Publication 760. American Society for Testing and Materials, Philadelphia, PA. pp. 209-304. 1981.

APPENDIX A

ANNOTATED BIBLIOGRAPHY

Anderson, D., K. Brown, and J. Green. Effect of Organic Fluids on the Permeability of Clay Soil Liners. In: Land Disposal of Hazardous Waste. Proceedings of the Eighth Annual Research Symposium. EPA-600/9-P2-002. USEPA, Municipal Environmenal Research Laboratory, Cincinnati, OH. 1982.

Report evaluates the permeability of four compacted clay soils when exposed to chemicals representative of four classes of organic fluids found in hazardous waste. Since permeability remains the primary criterion for evaluating the suitability of clay lines for the lining of hazardous waste disposal facilities, results indicate the need to test the permeability of prospective clay liners using the leachate to which they will be exposed. Laboratory investigations of the influence of organic chemicals on the properties of clay indicate tha organic fluids can substantially increase the permeability of compacted clay soils.

API. American Petroleum Institute. API Specification for Materials and Testing for Well Cements. API Spec 10. American Petroleum Institute, Washington, DC. 1982.

The purpose of this specification is to provide standards for well cements, well cement additives, and well cement testing procedures. Specification requirements are detailed for sampling and preparation of slurry. Specification tests address: soundness and fineness, determination of free water content of slurry, strength, thickening time, and atmospheric pressure consistometer. Individual sections are devoted to bentonite, barite, fly ash, marking, packaging, and storage, and inspection and rejection. Includes appendices.

Baker, W.H. (ed.) Proceedings of the Conference on Grouting in Geotechnical Engineering. American Society of Civil Engineers, New York, NY. 1982.

This is a publication of proceedings from the 1982 Conference in Geotechnical Engineering sponsored by the American Society of Civil Engineers. The 63 papers included represent 12 countries and deal with the pertinent advances in grouting materials and technology that have occurred throughout the world over the past decades. The conference was comprised of 12 sessions addressing the following topics: materials for cement and mortar grouts; dam grouting technology; applications; design and control; chemical

grouts materials, technology, and applications; behavior of chemically grouted soil; grouting for tunnels, shafts, and mines; and grouting testing, control, applications, and alternatives.

Bowen, R. Grouting in Engineering Practice. 2nd ed. John Wiley and Sons, NY. 1981.

Text examines various grout types, paying particular attention to two important categories: cement and clay-cements in water and chemical solutions. The techniques for application as well as specifications for utilization of different grouts is discussed. Book includes case histories as well as several new topics which did not appear in first edition. Also contains expanded glossary.

Herndon, J. and T. Lenahan. Grouting in Soils. Vol. One, A State-of-the-Art Report. FHWA-RO-76-26. Halliburton Services. Prepared for: USDOT, Federal Highway Administration, Washington, DC. 1976.

Report summarizes present grouting technology applicable to soils, from theory to field practices. Particular applications are given for cut-and-cover construction and soft ground tunneling. Includes: summary of patents applicable to grouting; list of grouting specialists, material, and equipment suppliers; bibliography of publications; and unpublished case histories of grouting jobs. Notes distinct differences between grouting performed in the United States and that performed in Europe. Contains summary and recommendations for improvements in the grouting field.

Herndon, J. and T. Lenahan. Grouting in Soils. Vol. II. Design and Operations Manual. FHWA-RO-76-26. Halliburton Services. Prepared for: USDOT5, Federal Highway Administration. Washington, DC. 1976.

Manual provides guidelines for design and conduct of soil grouting operations, from the selection of the grout and the design of the injection pattern to construction contol methods and evaluation of the completed treatment. This report emphasizes grouting applications associated with excavation and tunneling in an urban environment. Three general grouting techniques (permeation, void filling, and compaction) are described. Details are given on the following applications: groundwater control, sand stabilization, soil strengthening, backpacking, tunnel liners, leak repairs, and tieback anchorages.

Hurley, C. and T. Thornburn. Sodium Silicate Stabilization of Soils--A Review of the Literature. UILU-ENG-71-2007. University of Illinois, Urbana, IL. 1971.

This report consists of an annotated bibliography and summary review of the important literature on the use of sodium silicates in soil stabilization processes. Annotations are given for approximately 90 articles published between 1931 and 1965. On the basis of these articles the authors have summarized pertinent information on stabilizer properties, reaction mechanisms, injection methods of soil solidification, preparations of stabilizer-soil mixtures, use of sodium silicates as dustproofers and waterproofers, and their use as secondary additives with other stabilizers. Where warranted, conclusions have been drawn regarding the conditions under which sodium silicates appear to have potential value in the soil stabilization field.

Neville, A. Properties of Concrete. 2nd ed. John Wiley and Sons, New York, NY. 1973

The text provides a complete overview of Portland cement from its history to its manufacture. Addresses chemical composition and such physical properties as: hydration, setting, fitness, structure, volume, and strength. Includes detailed discussion on different types of cements. Incorporates information on current research and development and deals with some topics not included in first edition.

Office of the Chief of Engineers. Engineering and Design: Laboratory Soils Testing. EM 1110-2-1906. Department of the Army, Washington, DC. 1970.

Manual presents recommended testing procedures for making determinations of the soil properties to be used in the design of civil works projects. Appendices address physical characteristics of soils. Other chapters are devoted to soils tests, including permeability, consolidation, swell and swell pressure, and triaxial compression.

Tallard, G.R. and C. Caron. Chemical Grouts for Soils. Vol. I. Available Materials. FHWA-RD-77-50. Soletanche and Rodio, Inc. Prepared for: United States Department of Transportation, Federal Highway Administration, Offices of Research and Development, Washington, DC. June 1977.

Research involves the search for more economical grouts not dependent on petroleum. Based on the nature of the major component, a general classification of chemical grouts has been proposed. Factors forming the basis of evaluating grout materials include: permeability, strength, toxicity, durability, and injectability. A selected number of grouts have been tested for possible improvement, with lignochrome gels and furan resin deriviatives showing the most promise. This volume addresses the classification and evaluation of grouts, aqueous and colloidal solutions, non-aqueous grouts, emulsions, and products reacting with the ground.

Tallard, G.R. and C. Caron. Chemical Grouts for Soils. Vol. II. Engineering Evaluation of Available Materials. FHWA-RD-77-51. Soletanche and Rodio, Inc. Prepared for: United States Department of Transportation, Federal Highway Administration, Offices of Research and Development, Washington, DC. June 1977.

Examines more economical grouts not directly dependent on petroleum. Based on the nature of the major component, a general classification of chemical grouts has been proposed. Factors of evaluation include: injectability, permeability, setting time, strength of pure grout, strength of grouted soil, durability, and toxicity. Of a selected number of grouts which were tested for possible improvement, lignochrome gels and furan resin derivatives are particularly promising. This volume discusses testing requirements, proposed standard testing procedures, properties of promising grout materials, and evaluation of those materials.

Office of the Chief of Engineers. Engineering and Design: Chemical Grouting. EM 1110-2-3504. Department of the Army, Washington, DC. 1973.

Manual provides guidance and information regarding the use of chemical grouts, and for planning, executing, analyzing, and evaluating chemical grouting operations. Chemical grout materials and grouting equipment are described and methods of injection are presented. Provisions of this manual are applicable to Corps of Engineers concerned with civil works design and construction. Addresses the planning procedures of a chemical grouting program.

APPENDIX B
GROUT MANUFACTURERS/SUPPLIERS INFORMATION

TABLE B-1
PRODUCT MANUFACTURERS AND SUPPLIERS

Type of Grout	Product Name	Manufacturer or Supplier
Acrylamide	AC-400	Geochemical Corporation
	AV-100	Avanti International
	Injectite® -80	Penetryn Restoration
	Rocagil	Rhone Progil Company (France)
	Q-Seal	Cues, Inc.
Bentonite	Akwaseal	Federal Bentonite
	Imclay	International Minerals and Chemicals Corporation
	Volclay	American Colloid Co.
Epoxy	Ancamine, MCA	Pacific Anchor
	Epon	Shell Chemical
	Epotuf	Reichhold Chemicals, Inc.
	Five Star	U.S. Grout Corporation
Phenolic	Geoseal	Borden Chemical (Great Britain)
	Rogacil	Rhone Progil Company (France)
	Terraseal	Cellite, Inc.

TABLE B-1 (Continued)

Type of Grout	Product Name	Manufacturer or Supplier
Urea-Formaldehyde	Herculox (formulated for company use only)	Halliburton Services
Urethane	CR-250 and CR-202	3M
	Rokloc	Mobay Chemical
	TACSS	Takameka Komuten (Japan)
Silicate	Geloc (formulated for company use only)	Hayward Baker
	SIROC	No longer manufactured under this name
	Terraset	Celtite, Inc.
	(formulated for company use only)	Halliburton Services
	(formulated for company use only)	Raymond International
	(formulated for company use only)	SOLINC

TABLE B-2
LOCATION OF U.S. MANUFACTURERS AND SUPPLIERS

Avanti International
1275 Space Park Drive
Houston, Texas 77058
713-333-5430
Contact: F. David Magill

American Colloid Company
Environmental Products Division
5100 Suffield Court
Skokie, Illinois 60077
312-966-5720

Celtite, Inc.
Cleveland, Ohio 44133
216-237-3232
Contact: Tony Plaisted

Cues, Inc.
3501 Vineland Road
Orlando, Florida 32805
305-849-0190

Federal Bentonite
1002 Greenfield Road
Montgomery, Illinois 60538
910-232-0759
Contact: Bruce Beattie

Geochemical Corporation
162 Spencer Place
Ridgewood, New Jersey 07450
201-447-5525

Halliburton Services
Duncan, Oklahoma 73533
405-251-3760

Hayward Baker Company
1875 Mayfield Road
Odenton, Maryland 21113
301-551-8200
Contact: Joseph Welsh

TABLE B-2 (Continued)

International Minerals and Chemical Corporation
666 Garland Place
Des Plaines, Illinois 60016
312-296-0600

Mobay Chemical Corporation
Plastics and Coatings Division
Pittsburg, Pennsylvania 15205
412-788-1458
Contact: Kirk McCabe

Pacific Anchor Chemical Corporation
Richmond, California 94804
415-529-1020

Penetryn Restoration
Division of BPR Corporation
Knoxville, TN

Raymond International, Inc.
6825 Wertfield Avenue
Pennsauken, New Jersey 08110
609-667-3323
Contact: Dick Colle

Reichhold Chemicals, Inc.
RCI Building
White Plains, New York 10602
617-475-6600

SOLINC
Soletanch and Rodio, Inc.
6849 Old Dominion Drive
McLean, Virginia 22101
703-821-6727
Contact: Edmond Cardoza

U.S. Grout Corporation
401 Stillson Road
Fairfield, Connecticut 06430
203-336-7900

TABLE B-2 (Continued)

3M Center
Adhesives, Coatings and Sealers Division
St. Paul, Minnesota 55144
612-733-1110
Contact: Joe Gasper